QUALITATIVE CHEMICAL ANALYSIS

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ORGANIC AND INORGANIC

BY

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FIFTH EDITION

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PREFACE TO FIFTH EDITION

In producing the fifth edition of this book, every endeavour has been made to bear in mind the original objectives of the late author. In particular, special attention has been given to the dove-tailing of theory and practice, and to the inclusion only of tested methods.

The whole book has been thoroughly revised, the reactions have been brought up-to-date, and a number of additions have been made in order to introduce the student to modern trends in qualitative analysis. Thus, for example, the elements of micro-analysis, which are of considerable educational value (particularly in promoting neatness and clear thinking and in the acquisition of laboratory technique), are discussed in both the inorganic and organic sections.

Crystal tests and drop reactions, many of them involving the use of modern organic reagents, are given for most of the inorganic ions. These tests are usually very sensitive, and will be found of great value to the student later in his career, and here again the technique involved may very profitably be acquired at the student stage. In the writer's experience many of them (e.g. tests for sodium and potassium, nickel and cobalt, etc.) are valuable confirmatory tests, although of course the habit of using them as "short-cuts" to avoid the group separations should be discouraged, at any rate, in the early stages.

The so-called "Rarer Elements" have also been distributed throughout the text in their appropriate groups, and the number dealt with has been extended, as twenty-five years of chemical history has in many cases made the term "rare" an anachronism. Methods of separation have been indicated, since these are usually neglected in books of this type, and this shortcoming is a subject of frequent comment among teachers of chemistry. Additions have also been made to the various organic sections, notably to that on the alkaloids.

It is hoped that these and the numerous other minor additions and alterations have resulted in a modern text-book of qualitative analysis which will be of use to the student from the time he starts analytical work at school, through his university studies, and subsequently in the many ramifications of science in which chemical analysis plays a part.

J. G.

LONDON, *March*, 1935

PREFACE TO FIRST EDITION

PROBABLY all teachers of chemistry are familiar with two classes of student: (1) *book students*, i.e. students who have obtained their knowledge of chemistry entirely by reading or by hearing lectures; (2) *laboratory students*, those who, by use of a merely outline book or chart, and by attention to details of experiment, have obtained the whole of their knowledge in the laboratory. The first class of student, if brought into the laboratory, is unable to carry out a single experiment without bungling. The second, although he may be able to carry out experiments with machine-like precision, from a sheet of instructions, is quite at sea when questioned upon the underlying theoretical principles.

One of the great difficulties in teaching chemistry is to get students to apply their theoretical knowledge to aid them in their practical work, and, on the other hand, to bring their practical knowledge to bear in the elucidation of theoretical problems. The theoretical knowledge is generally kept rigidly apart from the facts practically gained, so that the student loses all the mutual help which the two branches of study afford each other.

Recognising this difficulty, I have endeavoured to write a book in which theory and practice are more or less dovetailed. Perhaps the theoretical considerations are not quite so fully dealt with as some would desire; but it must be remembered that the book is a practical one, and is only

intended to contain sufficient theory to make practical chemical analysis clear, and, I trust, interesting. If, as I hope, the appetite of the student is whetted, and he "asks for more," then he can obtain it from theoretical text-books.

In writing the theoretical portions of this book, I have been much aided by the works of Professor Ostwald. In the practical part I have consulted the latest literature, and among other works Fresenius's "Qualitative Analysis" and Allen's "Commercial Organic Analysis."

No reaction has been included which has not been worked out by myself and assistants in the laboratory.

In conclusion, my best thanks are due to Dr. W. Semple, M.A., B.Sc., and Dr. J. E. Mackenzie, B.Sc., for their kind help in revising the sheets before they went to press, and for many valuable suggestions. My thanks are also due to Messrs. E. E. Cornick and A. R. Warnes for much help in testing many of the reactions. I also desire to thank Messrs. Longmans for kindly allowing me a number of proof copies for the use of my students during the time the book was passing through the press.

F. M. P.

November, 1900.

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PART I.

INORGANIC ANALYSIS.

CHAPTER I.

DRY REACTIONS.

In **qualitative analysis** two classes of tests are employed: (i) **dry reactions,** or tests applied to the solid material; (ii) **wet reactions,** or tests applied to the substance in solution.

The **dry reaction** tests are usually applied first, and the information thus obtained often greatly facilitates the application of the **tests in solution.**

In this chapter the methods employed in testing by means of **dry reactions** will be explained, and will be taken in the following order:—

1. Action of heat alone on the substance.
2. Blowpipe reactions.
3. Match tests.
4. Film tests.
5. Flame colorations and the spectroscope.
6. Borax beads.
7. Other dry reactions.

1. Action of Heat on the Dry Substance.—Much may often be learned simply by heating the dry substance in a glass test-tube; *e.g.* the substance may **sublime,** or may be decomposed and give off coloured vapours, or the colour of the substance may change. The two following examples will serve as illustrations:—

(*a*) **Sublimation.**—Place a small quantity of **ammonium chloride** in the bottom of a glass tube three inches long, about a quarter of an inch wide, and closed at one end. Heat the end of the tube in the flame of the Bunsen burner; white

vapours will be given off, which will condense, *i.e.* "sublime," on the cool parts of the tube.

(*b*) **Decomposition and Sublimation.**—In another tube heat a little red **mercuric oxide.** The red colour becomes darker and darker, and finally almost black, while on the cool portions of the tube a grey deposit of metallic mercury collects, forming into small globules when rubbed with a glass rod. If a glowing splint of wood is held in the mouth of the tube, it bursts into flame, showing that oxygen gas is being evolved owing to the decomposition of the mercuric oxide.

$$2HgO = 2Hg + O_2$$

On cooling again, the undecomposed mercuric oxide gradually becomes lighter in colour until, when quite cold, it resumes its original appearance.

This change in colour, due to heating, is a **physical** change.

2. **Blowpipe Reactions.**—The use of the blowpipe is very important where gas or the Bunsen burner is not available. The flame of an oil or spirit lamp, or of a Bunsen burner with a blowpipe tube, is used as follows:—

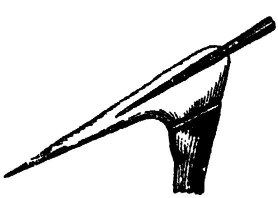


FIG. 1.

Hold the nozzle of the blowpipe just outside the flame (Fig. 1), and blow gently and steadily from the cheeks. The jet is partially luminous, owing to the presence of unburnt carbon, and is called the **reducing flame.**

To obtain the **oxidising flame,** hold the nozzle of the blowpipe in the centre of the flame (Fig. 2). The jet is now non-luminous, like the Bunsen flame, and contains no unburnt carbon. The use of the **reducing** and **oxidising** flames is illustrated by the two following examples:—

(*a*) Place a little **lead monoxide** (litharge) in a small hollow on a piece of charcoal, and direct the reducing flame on to it. The oxide becomes reduced, and small bright beads of metallic lead are obtained. The reducing gas and unburnt carbon in

the flame, together with the red-hot charcoal, combine with the oxygen of the lead oxide, with formation of **carbon monoxide.**

$$PbO + C = Pb + CO$$

(*b*) Place a small piece of **lead** in a small hole scooped out in the charcoal, and direct the extreme tip of the oxidising flame upon it; the lead becomes oxidised, and the oxide is deposited on the cooler portions of the charcoal, forming a yellow **incrustation** or **film.**

$$2Pb + O_2 = 2PbO$$

Since the introduction of the Bunsen burner, it is seldom necessary to employ the blowpipe in ordinary qualitative analysis. Much practice is required before the results obtained can be depended upon. Indeed, many students are never able to successfully use the blowpipe. Since, with a little practice, the following reactions are easily interpreted, and moreover do not take so long to carry out, ***the student is recommended to employ these reactions instead of those of the blowpipe.*** As, however, the blowpipe is still employed by many chemists, the blowpipe reactions are included among the other dry reactions.

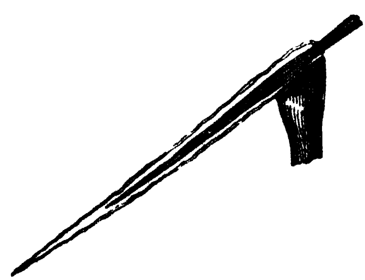


FIG. 2.

The Bunsen Burner.—Before describing the manner in which the dry reactions are carried out, it will be necessary to explain the structure of the flame of a Bunsen burner.

The flame of the burner (Fig. 3) may be divided into three chief divisions: (1) the dark **central zone,** *a*, *a'*, *a''*, which is a mixture of unburnt gas and atmospheric air; (2) the **flame mantle,** *b*, or zone of complete combustion; (3) the **luminous point,** B, which is produced by partially closing the air-holes at

the bottom of the burner. It should *not* be visible when the holes are entirely open.

The bottom of the flame, A, has comparatively a very low temperature. The **zone of fusion**, or the hottest portion of the flame, is at E, where the flame mantle is thickest. D is called the **lower oxidising flame**; here there is an excess of oxygen. G is the **higher oxidising flame**: it contains an excess of oxygen, but is not so hot as D. The reducing flame is at K, in the middle of the luminous tip; it contains finely divided incandescent carbon and partially burnt gas, but no free oxygen. H, H, is a metal chimney standing on the star support S. It is employed to keep the flame from flickering with draughts; it should always be used when carrying out the film tests.

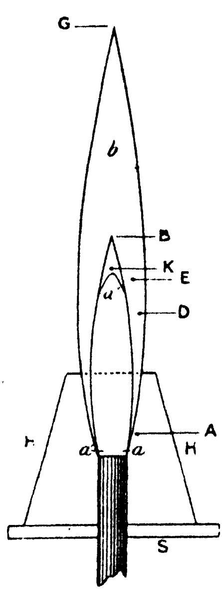


FIG. 3.

3. Match Tests.—Cut the head off a stout wooden match, or obtain a splint of wood about the same size as a match.† Take a lump of crystallised sodium carbonate (washing soda), hold it in the flame so that it partially fuses, and rub the fused salt over about three-quarters of the length of the match. Now heat the match in the flame, at the same time rotating it. As soon as the match is covered with dry salt, repeat the first operation, in order that the wood may be thoroughly covered with the sodium carbonate, and again heat, with continual rotation, until the end of the match is thoroughly charred and the sodium carbonate fuses on it.‡ Now mix a

† Very thin matches are liable to break in the carrying out of the experiment. Matches about 6 cm. long and 3 mm. thick, or pieces of wood about the same thickness, should be employed.

‡ These tests are more readily carried out and the charred wood is less likely to break off, if the splints are first impregnated with a mixture of sodium

small portion of copper sulphate with a little melted sodium carbonate on a watch glass, and with the hot end of the match pick up a portion about the size of a pin's head. Hold it in the luminous tip of the flame. The copper sulphate becomes reduced to metallic copper. Hold it for about half a minute in the cooler non-luminous portion of the flame. Gently crush the carbonised end with a pestle in a mortar containing a little water, and wash away the light portions of the charcoal, when metallic copper will be left behind. Repeat this experiment, using silver nitrate, lead or iron oxide, etc., etc.

4. **Film Tests.**—Take a porcelain basin, glazed outside, and about half full of cold water. Hold this immediately over the luminous point B of the Bunsen flame. The point should be made just visible by partially closing the air-holes. If any carbon is deposited upon the porcelain, air must be admitted until a deposit is no longer produced.

Having arranged the flame correctly, take a thread of asbestos, moisten the end with water, pick up with the moistened end a trace of **arsenious oxide,** and heat it in the luminous tip, at the same time holding the basin immediately over the luminous tip of the flame. A black metallic film will be deposited on the porcelain. The film will be found to be sparingly soluble in 20 per cent. **nitric acid,** but will dissolve at once if touched with a drop of a solution of bleaching powder.

Now take a fresh portion of the arsenious oxide on the asbestos thread, and again hold it in the same portion of the flame, but this time hold the dish just outside the upper oxidising flame G. A white deposit of arsenious oxide will be produced on the porcelain. By looking sideways at the bottom of the dish, the portion where the oxide film is deposited will be

carbonate and alum. This may be done by boiling them for about half an hour in a nearly saturated solution of 2 parts sodium carbonate and 1 part alum. After drying they are ready for use. It is a good thing to keep a stock of splints prepared in this manner. These splints must be treated with the fused sodium carbonate as above described.

seen to have a dull appearance. The first film is the **metallic film**, the second the **oxide film.** On p. 198 a table giving various tests for the metallic and oxide films will be found.

The **iodide film test** (p. 198) is best carried out as follows: Dissolve some iodine in alcohol, and dip into the solution a small bundle of asbestos wired on to a glass rod and reserved for this purpose. Ignite the moistened asbestos, and, when the flame begins to go out, hold it under the oxide film (the basin should contain water, because some of the iodide films are readily volatile). Or, better still, hold the basin over a 2-oz. wide-mouthed bottle containing fuming hydriodic acid.

The **sulphide film** (p. 198) can be produced by adding a drop of ammonium sulphide to the **oxide film** by means of a glass rod or a capillary tube, or by fitting a small flask up like a wash bottle, both tubes being bent at right angles. A little ammonium sulphide solution is poured into the flask, and on blowing down the long tube which passes below the surface of the liquid, the vapour is directed against the film, which is held in front of the opposite tube. The first method gives very satisfactory results if only very small quantities of the sulphide are added.

The iodide and sulphide film tests are applied to the metallic film in the case of mercury, which gives no oxide film. The student should repeat the above exercise, with the metals mentioned in the table, p. 198.

5. Flame Tests.—Take a fine platinum wire, about three inches long, and fuse one end into a piece of glass rod or tube, and clean it in the manner described below. Moisten the wire with a little pure concentrated hydrochloric acid contained in a watch glass, dip it into a little powdered **potassium chloride,** a small portion of which will adhere, and when the wire with the potassium chloride is introduced into the lower part of the flame mantle, the potassium chloride volatilises and colours it a violent blue.

Thoroughly clean the wire, by alternately boiling it in a little concentrated hydrochloric acid, and heating it in the

flame until the flame is no longer coloured. Again moisten with concentrated hydrochloric acid, as already described, and take up a little **strontium chloride.** When introduced into the hottest portion of the flame mantle at E, strontium chloride colours the flame a brilliant crimson. As potassium volatilises at a lower temperature than the salts of most other metals which give flame colorations, its presence may often be shown, even in the presence of other substances, by introducing the platinum wire into the cooler portions of the flame mantle near the base.

When a little potassium and sodium chlorides are mixed together, and brought into the flame of the Bunsen burner, the golden yellow imparted by the sodium completely masks the violet of the potassium. If, however, the flame so coloured is viewed through a thick piece of blue glass or a hollow glass prism filled with a solution of indigo, the yellow rays are cut off, and only those due to the potassium are visible, the flame appearing violet-red in colour.

6. The Spectroscope.—By means of the spectroscope the flame reactions may be rendered much more delicate, and the metals are more easily detected, even when several are present together. If a metallic salt is volatilised, as just described, and the flame is viewed through a spectroscope, then certain lines which are distinctive for each metal will be seen. Introduce separately small portions of the salts of **sodium, potassium, calcium, barium, strontium,** and **lithium** into the Bunsen flame by means of a piece of platinum wire, examine the coloured flame with a spectroscope, and compare the results thus obtained with the coloured diagram at the beginning of the book.

In using the spectroscope, some little practice is necessary, and it will be found advisable to clamp the glass end of the platinum wire in a stand, so that the wire remains steady. The spectroscope should also be clamped. A direct-vision spectroscope is the most convenient for laboratory use. It should not, however, be too small, otherwise the field obtained is too short.

Small hand- or pocket-spectroscopes are also obtainable, and are very simple to use, one end being pointed at the flame, while the eye is applied to the other. Although the component lines of the light are shown very satisfactorily, there is no scale to read off the corresponding wave-lengths and identification is therefore not quite so simple. Once, however, a rough idea of the nature of the substance has been obtained, a little of the pure salt may be heated in another flame and the two spectra compared. Some spectroscopes make provision for viewing both spectra at the same time and for producing the spectra next to one another so that lines common to both are easily identified.

7. Borax Bead Tests.—Take a clean platinum wire which has been fused into a piece of glass tubing, and make a small loop at the end. Heat the wire in the Bunsen flame, and dip it while hot into powdered **borax** ; some borax will adhere to the wire. Now heat in the hottest part of the Bunsen flame. The borax will swell up, and then become fluid, finally fusing to a clear bead. With the hot clear bead touch a small crystal of a **cobalt salt,** and again fuse in the hottest part of the flame. The bead becomes coloured a brilliant sapphire blue, the colour being the same whether the bead be held in the oxidising or reducing flame.

Manganese salts produce an amethyst violet bead in the oxidising flame, and a colourless bead in the reducing flame. Other metallic salts also produce characteristic colorations, which are described under the reactions of the particular metal.

Microcosmic salt (sodium ammonium hydrogen phosphate), $Na(NH_4)HPO_4$, is also used for forming beads. Since, however, it is more readily fusible, these are not so easily held in the platinum loop as is the borax bead.

The reactions on which these tests depend may be explained in the following manner:—

The borax when fused is resolved into **sodium metaborate** and **boric anhydride.**

$$Na_2B_4O_7 = 2NaBO_2 + B_2O_3$$

The metallic oxide then unites with the metaborate and with the boric anhydride, forming an **orthoborate** and a **metaborate,** *e.g.*—

$$NaBO_2 + CuO = CuNaBO_3$$
$$B_2O_3 + CuO = Cu(BO_2)_2$$

When microcosmic salt is fused, **sodium metaphosphate, ammonia,** and **water** are the products.

$$Na(NH_4)HPO_4 = NaPO_3 + NH_3 + H_2O$$

The metallic oxide combines with the sodium metaphosphate and produces an **orthophosphate,** thus—

$$NaPO_3 + CuO = CuNaPO_4$$

8. **Other Dry Reactions.**—Some substances, when heated on charcoal in the blowpipe flame, then moistened with a solution of cobalt nitrate, and again heated, give characteristic coloured masses—*e.g.* **zinc** salts green, and **magnesium** salts pink.

These reactions may also be carried out as follows :—

Moisten a piece of filter paper with a solution of zinc sulphate and then with a drop of cobalt nitrate. Dry over the Bunsen flame and ignite. The ashes of the paper will be coloured green, especially at the edges.

The Draught Tube.—Take a glass tube about four inches long and a quarter of an inch wide, place in the middle of it a small quantity of mercury sulphide, and heat this portion of the tube in the Bunsen flame. The tube should be slightly inclined. Mercury will condense on the cool upper portion of the tube, and a smell of sulphur dioxide will be perceptible. Sulphides, when thus heated or " roasted " in a stream of air, are decomposed into the metal or its oxide and sulphur dioxide, *e.g.*—

$$HgS + O_2 = Hg + SO_2$$
$$2PbS + 3O_2 = 2PbO + 2SO_2$$

The student is *urged* to make a very careful study of the dry **reactions**, the importance of which, as an aid to analysis, cannot well be over-estimated.

A low-power **microscope** or a magnifying **lens** is frequently of great help in the laboratory. It is often possible to distinguish the different ingredients in a mixture by their use, and this is of very material help in the subsequent analysis.

CHAPTER II.

REACTIONS IN SOLUTION.

THE applications of dry reactions are necessarily limited. The difficulty of recognising substances in a mixture by means of dry tests alone, which usually take place at high temperatures, renders it necessary to apply so-called "wet-reactions," or reactions in solution, by means of which not only may the elements present be detected, but also, in many cases, the state of combination in which they are present may be determined. But even with reactions in solution it is often a matter of great difficulty, sometimes of impossibility, to decide in what form or combination the elements occur in the original mixture. Thus, when a solution of common salt is added to a solution of potassium nitrate, no sign of chemical reaction is observable. Yet this solution is similar in every respect to one obtained by mixing together solutions of sodium nitrate and potassium chloride. Indeed, if equivalent proportions of the two pairs of salts in question be dissolved in equal volumes of water, the resulting solutions are absolutely identical in their reactions.

Many such instances might be given. It is therefore evident that, even by means of reactions in solution, we cannot say what the components of a mixture originally were—whether, for example, the above-mentioned mixture contained, in the first place, sodium chloride and potassium nitrate, or sodium nitrate and potassium chloride. It must, however, be noted that a physical examination of the original solid, and an intelligent combination of dry tests with tests on solutions, often supply this information.

As the chief reactions and tests in analytical chemistry are

produced in solutions, a short account of the theoretical considerations involved will make it easier for the student to follow out and understand many of the reactions which may at first sight appear very complicated.

Theory of Solution.—In solution, salts, acids, and bases do not behave as complete molecules, but are resolved into simpler components, and, in analysis we deal only with these components instead of with the many compounds which may result from combinations of these simple components. Thus the reactions of any soluble salt of a particular metal with a particular reagent are the same, no matter what salt of the metal is employed; *e.g.* the chloride nitrate, bromide, or any other soluble salt of barium, all give a white precipitate with sulphuric acid, or a yellow one with potassium chromate. Likewise all the soluble salts derived from a given acid react similarly with the same reagent, independently of the metal contained in the salt. Thus the sulphates of potassium, magnesium, zinc, etc., all give the same white precipitate on addition of barium chloride.

It was the observation of these facts of the formation of salts by the inter-action of bases and acids, and of the decomposition of compounds in solution by the electric current (electrolysis) which led Berzelius to formulate his theory of the constitution of salts. According to this theory, a salt is composed of a positive or basic portion, and a negative or acid portion, both of which retain to a modified extent their individual existence in the molecule; the basic portion being **a basic oxide,** the acid portion an **acid anhydride.** The nomenclature associated with this view still persists, more especially in treatises on chemical analysis and in analytical reports. Thus, **potassium sulphate** is still called **sulphate of potash,** and **sodium nitrate, nitrate of soda.** The Berzelius formulæ for these salts, according to the present atomic weights, would be written for sulphate of potash $K_2O \cdot SO_3$, and for nitrate of soda $Na_2O \cdot N_2O_5$.

The theory of the constitution of salts now generally accepted has resulted from a closer study of electrolytic reactions. This theory also assumes salts to consist of two parts: one a metal or metallic radical, the other an acid radical. These parts exist independently of each other in dilute solutions, the metallic radical being positively charged, while the acid radical has a corresponding negative charge.

The difference between the new and the old views is best shown by considering the accuracy with which they represent what happens during the electrolysis of a salt solution. According to the original theory the decomposition of a salt was effected by the expenditure of electrical energy, but the latter says the salt is already split up ("ionised") in water. The electric current merely causes the radicals which are positively charged to move towards a negatively charged terminal, while the negatively charged radicals migrate towards the positively charged terminal. Since the charges on the electrified radicals are then neutralised, they are thus set free to form new whole atoms and molecules.

The nomenclature suggested by Faraday for the old theory expresses the modern interpretation so well that it is retained. Faraday called the radicals **ions** (travellers), and, seeing that the positively charged ions move with the positive current, they are called **cations**, while the negatively charged ions, having to travel against the positive stream, are called **anions**. The cations give up their positive charge to the negatively charged terminal or **cathode**, and the anions give up their negative charge to the positively charged **anode**. Thus, *e.g.* the molecule of **cupric chloride**, $CuCl_2$, is supposed to be more or less dissociated or **ionised** † in solution (according to the concentration) into a positively charged cation $Cu^{\cdot\cdot}$, coloured blue, and into two odourless and colourless anions, Cl', the two together having a charge of negative electricity equivalent to

† "Electrolytic dissociation" is rather an unfortunate name, as it seems to suggest that the dissociation is due to electrolysis. "Ionisation" seems preferable.

the positive charge on the one $Cu^{\cdot\cdot}$ cation. When electrodes are placed in a solution containing these ions, the blue $Cu^{\cdot\cdot}$ cations are attracted to the cathode, and, on having their positive charges neutralised, they appear as red **copper** molecules. Similarly, the Cl' anions are attracted and discharged by the anode. Each pair of Cl' ions unites to form a chlorine molecule recognisable by the colour and odour.† The electrolysis of other salts may be interpreted in a similar manner, though they are often complicated by so-called secondary reactions. The current of electricity which passes through a solution is, in fact, conveyed by the ions. Substances which are ionised in solution, and are therefore capable of carrying electric currents, are called **electrolytes.** The more a substance is ionised the greater is the electrical conductivity of its solution. Electrolytes are more completely ionised in dilute solutions than in concentrated solutions.

Upon the degree of ionisation of an acid (or base) depends the electric conductivity and its chemical activity. In strong acids such as **hydrochloric acid** and **sulphuric acid**, the degree of ionisation is great, whereas such weak acids as **hydrocyanic** and **silicic acid** are hardly dissociated to a measurable extent, consequently they are very poor conductors of the electric current. Again, **sodium** and **potassium hydroxides** are powerful bases, and exist in solution largely as ions, while **ammonium hydroxide** is only feebly dissociated. In acids the characteristic ion is the **hydrogen cation** $H^{\cdot}$, in bases it is the **hydroxyl anion** OH'.

This distinction between strong and weak acids and bases is of considerable importance in analytical work and in industry. Since strong acids are ionised to a relatively great extent they will produce a large number of hydrogen ions, and the strength of an acid in this sense may be expressed as its **hydrogen ion concentration** ($C_{H^{\cdot}}$); similarly, the strength of a base is defined by the **hydroxyl ion concentration** ($C_{OH'}$). It will

† Atoms and molecules must therefore not be confused with ions, which are electrically-charged atoms, or parts of molecules known as radicals.

be appreciated that " strength " in this sense differs from that obtained by titration, which after all is the measure of the total concentration of acid or base present in a given volume, irrespective of whether it is strong or weak. Ionic concentrations, therefore, measure potency rather than amount, *e.g.* a 0·1 *N* solution of hydrochloric acid contains many more hydrogen ions and its acidic properties are much more pronounced than a 0·1 *N* solution of acetic acid; a comparison of their tastes provides an excellent demonstration of this. Finally, the important term **p_H value** should be mentioned, since it is a conception which is playing a considerable part in modern chemistry, and it provides a very convenient way of expressing hydrogen ion concentrations, particularly if they are very small. p_H *value is defined as the logarithm of the reciprocal of the hydrogen ion concentration* ($\log 1/C_{H^{\cdot}}$). Thus, the p_H value of a 0·001 *N* solution of a fully ionised acid is 3. The p_H value of pure water is approximately 7, so that p_H values below this correspond with acid solutions and p_H values higher than 7 with alkaline solutions.

Hydrolysis.—Even water itself is very feebly ionised into the cation $H^{\cdot}$, and the anion OH', and although it is very slight, it plays a very important part in the **hydrolysis** of the salts of weak acids and bases, *i.e.* salts of acids and bases which when once produced tend to revert to the non-ionised condition. This may be due either to the base being weak, to the acid being weak, or to both. In the first case, the salts will have an acid reaction. In the second case, they will show an alkaline reaction, *e.g.*—

$$(Fe^{\cdot\cdot\cdot} + 3Cl') + 3(H^{\cdot} + OH') = \overbrace{\underset{\text{not ionised}}{Fe(OH)_3} + \underset{\text{ionised}}{3(H^{\cdot} + Cl')}}^{\text{acid reaction}}$$

$$(K^{\cdot} + CN') + (H^{\cdot} + OH') = \overbrace{\underset{\text{not ionised}}{HCN} + \underset{\text{ionised}}{(K^{\cdot} + OH')}}^{\text{alkaline reaction}}.$$

From the foregoing statement, it is evident that " salts do not exist, as such, in aqueous solution, but are dissociated more

or less completely into their constituents, or ions"; † and it therefore follows **that, in analysis most reactions in solution are reactions of the ions. And that in so-called double decomposition reactions it is the ions and not the molecules which react.**

Hydrate Theory of Solution.—The ionic theory of solution is an exceedingly useful working hypothesis, and it certainly elucidates many analytical reactions which, without its help, are difficult to explain. There are, however, those who do not accept the theory, and prefer to consider that when a salt is added to water, a series of hydrates is produced, the complexity and amount of hydration of which increase with dilution.

There is probably truth in both theories, and in *strong* solutions we may have both **hydrated molecules**—thus Na_2SO_4, xH_2O, **and ions**. As the dilution increases, however, the number of hydrated molecules becomes fewer, and finally the solution contains only hydrated ions. These assumptions do not interfere with or modify the above statement "that in analysis most reactions in solution are reactions of the ions. . . ."

There are several other theories, one of which is mentioned in connection with the deduction of the Law of Mass Action on p. 23. Others completely oppose the ionic notion. It will be noted that we have assumed that the active masses are equal to the concentrations of the reacting substances, and this involves the assumption that the molecules are "free," and do not occupy any appreciable volume themselves. This may be justified with weak electrolytes, but strong electrolytes do not obey the law of mass action, and it is necessary to multiply the concentrations by an arbitrary factor (known as the "activity") to make them do so (Lewis's theory). The activity, therefore, is simply a correction.

Reactions in solution will now be considered under the following heads—**Precipitation, Evolution of Gases, Colour-changes.**

† Arrhenius.

Precipitation.—If one solution contains an anion, and another a cation, which by their union may give rise to an insoluble salt, then this insoluble substance will be precipitated (*i.e.* thrown out of solution) by the union of these two ions when the solutions are mixed. After carefully studying the solubility of various salts, and the mutual reactions of ions under the heading " Reactions of the Metals " and " Reactions of the Acids," the student will be able to judge whether a given ion or group of ions is present in a solution by adding to that solution another solution containing an ion which is capable of forming an insoluble compound with the ion or ions sought.

Thus silver chloride is practically insoluble in neutral and acid solutions, but is readily soluble in ammonium hydroxide. Moreover, it is the only white salt which acts in this way. It is composed of the cation $Ag^{\cdot}$† and the anion Cl'. If, then, the addition of a solution containing the anion Cl' to a certain solution produces a white precipitate readily soluble in **ammonium hydroxide**, and reprecipitated by nitric acid, then the ion $Ag^{\cdot}$ is present in the latter solution. Again, if a solution containing the cation $Ag^{\cdot}$, *e.g.* silver nitrate, is added to an unknown solution, and produces the same white precipitate, then the presence of the anion Cl' is demonstrated. A solution of silver nitrate is therefore a reagent for the detection of the anion Cl'; and a solution containing the anion Cl', *e.g.* hydrochloric acid, is a reagent for the detection of the cation $Ag^{\cdot}$. But silver nitrate is *not* a reagent for the element chlorine ; thus silver nitrate gives no precipitate with a solution of potassium chlorate, because, in solution, potassium chlorate is dissociated into the cation $K^{\cdot}$ and the anion ClO'_3. Similarly, on adding **sodium hydroxide** to a solution of ferric chloride a reddish-brown precipitate of **ferric hydroxide** is produced. But on adding a solution of sodium hydroxide to

† The valency of the cation is represented by a (·) : thus, in ferrous salts the cation is $Fe^{\cdot\cdot}$, in ferric salts $Fe^{\cdot\cdot\cdot}$. The valency of the anion is represented thus (′), *e.g.* the anion of the ferrocyanides is $Fe(CN)_6''''$, that of ferricyanides $Fe(CN)_6'''$.

one of potassium ferrocyanide no precipitate formed. The ferric chloride produces in solution the cation $Fe^{\cdot\cdot\cdot}$ and three Cl' anions, but the molecule of potassium ferrocyanide is dissociated into the cations $4K^{\cdot}$, and the complex anion $Fe(CN)_6''''$. Sodium hydroxide is therefore a reagent for the trivalent ion $Fe^{\cdot\cdot\cdot}$, but not for the element iron.

It has already been stated that reactions are produced by interaction of the ions. From this it follows, therefore, that in writing equations it is only necessary to specify the ions. Thus, as has already been pointed out (p. 14), all the soluble salts of a given metal behave as if the metallic ion alone is present. For example: copper chloride, nitrate, or sulphate might equally well be employed for demonstrating the reactions of copper with various reagents (see p. 52), and therefore the equations can be expressed in terms of the cation $Cu^{\cdot\cdot}$ and of the anion of the reacting substance. *E.g.* the reactions 2, 3, and 4, on p. 53, might be more generally expressed as follows:—

$$(1) \qquad Cu^{\cdot\cdot} + 2OH' = Cu(OH)_2$$

$$(2) \qquad Cu^{\cdot\cdot} + S'' = CuS$$

$$(3) \qquad 2Cu^{\cdot\cdot} + Fe(CN)_6'''' = Cu_2Fe(CN)_6$$

Written as above, the equations make it clear that the ions react together to form un-ionised products, and, as these un-ionised substances are insoluble in water, a precipitate is produced.

Evolution of Gases.—The evolution of a gas often results when two solutions are mixed and an exchange of ions takes place. Thus, when sulphuric acid is added to a solution of common salt (NaCl), the ions $H^{\cdot}$ and Cl' are present together in the same solution. Their union will produce hydrochloric acid, but in dilute solution, such union does not take place. When, however, the solution is concentrated by evaporation, the hydrochloric acid is given off † owing to the combination

† It must not be supposed that because sulphuric acid will liberate gaseous hydrochloric acid from its salts, that it is a stronger acid than hydrochloric acid. In fact, the contrary is the case, the hydrochloric acid being expelled because it is more volatile than the sulphuric acid.

of the ions $H^{\cdot}$ and Cl'. In cases of feebly ionised acids such as hydrogen sulphide, the evolution of gas is much more marked, and takes place even in extremely dilute solutions, and the same applies to acids, such as carbonic acid, which is readily decomposed into carbon dioxide and water. The evolution of ammonia from ammonium salts on addition of sodium hydroxide is another example, the feebly dissociated ammonium hydroxide (p. 132) being decomposed into ammonia and water.

Colour Changes.—The colours of precipitates are often characteristic, and are thus of great importance in the recognition of the ions which form the precipitates. The change in colour of solutions is also of great use, some methods of testing in qualitative and quantitative analysis being based entirely on such changes. Changes in colour may either be due to ionisation, or to reversion to a non-ionised condition. The importance of litmus as an indicator to show whether a liquid is alkaline, acid, or neutral probably depends upon the fact that red litmus is a very feebly ionised acid, while blue is the colour of the litmus acid anion in the dissociated salt. When an acid neutralises an alkali, the $H^{\cdot}$ cations of the acid unite with the OH anions of the base to form un-ionised water. The ions which remain in solution are the anions of the acid and the cations of the base, *e.g.*—

$$(H^{\cdot} + Cl') + (Na^{\cdot} + OH') = \underset{\text{not ionised}}{HOH} + \underset{\text{ionised}}{(Na^{\cdot} + Cl')}$$

It follows, then, that as long as any OH' anions remain unannexed, the cation $H^{\cdot}$ of the litmus acid can unite with them to form water, and thus the blue litmus anion exists in the dissociated state. But the moment the least excess of free $H^{\cdot}$ cations appears, they unite with the blue litmus anion to form red undissociated litmus acid.

The red coloration produced by the addition of potassium thiocyanate to a solution of a ferric salt (p. 95) is attributed to the formation of non-ionised ferric thiocyanate, because

the CNS′ ion is colourless, while the ferric ion $Fe^{\cdot\cdot\cdot}$ is pale yellow.†

Many colour changes are due to the conversion of one ion into another. Thus the monovalent permanganate anion is a deep purple, while the divalent $Mn^{\cdot\cdot}$ cation is pale pink. Hence, when the permanganate anion $MnO_4{}'$ is reduced to the divalent $Mn^{\cdot\cdot}$ cation by the action of reducing agents, the colour disappears. Again, the green chromium salts are converted by oxidising agents to the yellow chromates, *i.e.* the green trivalent $Cr^{\cdot\cdot\cdot}$ cation becomes changed to the yellow $CrO_4{}''$ anion. Many such changes will be noticed in working through the reactions mentioned in this book.

For fuller information on the subject, the student should study Ostwald's " Foundations of Chemical Analysis," " The Measurement of Hydrogen Ion Concentration," by J. Grant, or Taylor's " Physical Chemistry."

Mass Action.—Many chemical reactions are reversible; that is, under certain conditions they will go in one direction and under other conditions in the opposite direction.

For example, when calcium carbonate is heated, carbon dioxide and calcium oxide are produced, but if the heating is carried out in such a way that the carbon dioxide gas is not removed, a portion of it unites with an equivalent proportion of calcium oxide to re-form calcium carbonate. Finally a point is reached at which the decomposition and re-formation of calcium carbonate take place at equal rates, and a so-called condition of equilibrium is produced. Such a condition is usually expressed as follows :—

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

If the carbon dioxide is removed the reaction goes from left to right only, but if the pressure of the carbon dioxide is increased, then the reaction proceeds more rapidly from right to left, and

† The brown colour of the solution of ferric chloride in pure water is due to hydrolytic production of feebly-ionised ferric hydroxide. See p. 17.

the amount of calcium carbonate remaining undecomposed is increased.

The law of mass action is based on the statement that *the velocity of the reaction at any instant is proportional to the active masses (or concentrations of the reacting substances).*

Barium sulphate is insoluble in most solvents, yet it can be partly decomposed by boiling sodium carbonate solution, soluble sodium sulphate and insoluble barium carbonate being formed. The reaction is reversible, and can be represented by the following equation :—

$$\underset{(\alpha - x)}{BaSO_4} + \underset{(\beta - x)}{Na_2CO_3} \rightleftharpoons \underset{x}{BaCO_3} + \underset{x}{Na_2SO_4}$$

Now, let the concentration (or number of molecules of barium sulphate per unit volume of the reacting mixture) at the beginning of the action be α, and that of the sodium carbonate be β. If at the end of any instant x molecules each of barium carbonate, and sodium sulphate are formed, then x molecules each of barium sulphate and sodium carbonate will have been decomposed, and the concentrations of the barium sulphate and sodium carbonate will be $\alpha - x$ and $\beta - x$ respectively.

Now, according to our definition of the law of mass-action, the velocity of the reaction between the barium sulphate and sodium carbonate at any instant will be proportional to $(\alpha - x)$ and also to $(\beta - x)$, so that if k_1 is a constant, it will equal $k_1(\alpha - x)(\beta - x)$. Similarly, the velocity of the reverse reaction between the barium carbonate and the sodium sulphate will be k_2x^2.

When equilibrium is produced these velocities are equal, therefore

$$k_1(\alpha - x)(\beta - x) = k_2x^2$$

or

$$\frac{(\alpha - x)(\beta - x)}{x^2} = \frac{k_2}{k_1} = \text{constant}$$

Now, if β is made very large, compared with α, then $\alpha - x$ will be very small, and α will become approximately equal to x. That is, if the concentration of the sodium carbonate is very

great, then the more of the barium sulphate will be converted into barium carbonate. The greatest concentration of β can be obtained by fusing barium sulphate with excess of sodium carbonate, and then the reaction from left to right is quantitative.

A similar process of reasoning shows that to remove the sodium sulphate formed when barium sulphate is fused with sodium carbonate, without any of the barium carbonate being reconverted into the sulphate, the fused mass must first be washed with very small quantities of water, and when most of the excess of the sodium carbonate has been removed, a solution of sodium carbonate must be employed, until the washings no longer contain SO_4'' anions (see p. 206).

The residue then contains all the barium, as barium carbonate free from sodium sulphate. The solution is a mixture of sodium sulphate and carbonate.

The deduction of the law of mass action is a general one, and may also be applied to similar reactions involving substances which are all soluble, and also to ionisation equilibria of the type shown on p. 20.

Filtration and Washing of Precipitates.—For purposes of filtration, the larger and more granular the particles of the precipitate are, the more rapid will the filtration be, and the more readily is the precipitate washed. If the particles are very small, they block up the pores of the paper, and thus render the process of filtration very tedious, and often very imperfect. It is therefore important that the precipitation be conducted in such a manner that the grains of solid matter may be as coarse as possible. When other considerations allow, precipitation is best conducted in hot solution; the solution in which the precipitate is suspended should then be allowed to stand in a warm place for some little time, and should again be boiled before filtering.† By digestion, especi-

† Water at 100° will filter about six times as rapidly as water at 0°. Whenever possible, solutions should therefore be filtered hot.

ally in hot solution, the granular structure of the precipitate develops, the reason being that the smaller grains tend to dissolve, while the larger grains increase in size as a result of a form of crystal growth and of aggregation with one another. The reduction in size and the consequent solubility of the smaller grains is traceable to the surface tension exerted between liquids and solids. This explanation presupposes that *no substance is absolutely insoluble*, a fact which has been proved by recent refinements in physical chemistry. When the precipitate is coarse-grained, filter papers with fairly large pores can be employed, and so, of course, filtration is much expedited. The filter paper should always be moistened before being used for filtering, otherwise the first portion of the filtrate is liable to be turbid.

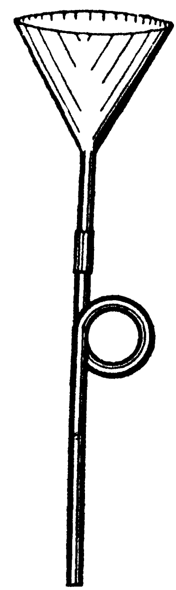


FIG. 4.

It is the force of gravity which causes the solution to pass through the filter paper. The force can be increased by decreasing the pressure below the funnel; this may be done by means of a vacuum pump, but it is not satisfactory for ordinary analytical purposes. The best method is to join on to the end of the funnel a long, narrow glass tube, bent as shown in Fig. 4.

The length of the column of liquid exerts hydrostatic pressure, but in order that the tube may be full of liquid, it must have a narrow bore, otherwise the liquid will simply run down the sides, and no pressure will be produced. On the other hand, the bore of the tube must not be too narrow, or else the surface tension will more than counterbalance the advantages gained. It is, further, most important that the filter paper should fit quite closely to the funnel, otherwise air will be drawn down between the paper and the walls of the funnel.

Washing the Precipitate.—Having transferred the precipitate to the filter paper, it must be washed to free it from adhering foreign matter which is present in the solution. When the whole of the solution has run through, it is washed with successive small quantities of water, each portion being allowed to drain through before the next is added. Where admissible, hot water should be employed, and it should be directed by means of a wash bottle upon the upper portion of the precipitate, in order to wash it down to the foot of the cone. Much time may often be saved, and the washing be more thoroughly effected, by a combination of decantation and filtration. The precipitate is allowed to settle, and the supernatant liquid poured on to the filter paper. Distilled water is added, and the operation is repeated several times; finally the whole of the precipitate is poured on to the filter, where it may be further washed, if necessary.

Colloidal State.—It sometimes happens that the precipitate tends to assume the colloidal state, that is, it tends to dissolve or to form very fine particles which are on the border-line between true solution and precipitation. Actually, they are electrically-charged, and therefore repel one another and will not aggregate, and they are so small that they will pass through the filter paper. A precipitate in this form is known as a **hydrosol** *e.g.* when hydrogen sulphide is added to or passed through a solution of an arsenate, the solution becomes yellow, but no precipitate is formed, and, on filtering this solution, all the arsenic passes through in the solution. Boiling will often cause precipitation of colloidal substances, or addition of salts, such as ammonium acetate, sodium, sulphate, etc., will effect the same purpose, and the resulting precipitate is known as a **hydrogel.** Some substances, again, though they may have been precipitated in a granular form, tend to become colloidal when brought into contact with pure water; as, for example, when being washed on the filter. When this happens, the filtrate becomes turbid towards the end of the operation, owing to the colloidal substance passing through the pores of

the paper. The pores may even finally become blocked, and render further washing almost an impossibility.

When a precipitated substance shows a tendency to assume the colloidal or hydrosol state, it should first be allowed to stand for some time in contact with the precipitant, and may, with advantage, be placed on a water bath. It should then be filtered as far as possible, by decantation, and, when permissible, washed with a strong solution of ammonium acetate, or nitrate, or sodium sulphate. In the arsenic group (p. 58), where both tin and arsenic sulphide have a tendency to become colloidal, these precautions should invariably be adopted; in addition, the hydrogen sulphide should be passed for about 5 minutes, and the procedure repeated on the filtrate in order to ensure that precipitation is complete, and so to avoid complications in the subsequent group separations (see Chapter III).

MICRO-METHODS.

Micro-methods serve several valuable purposes. Economy of material to be tested is an important one, particularly in analyses for commercial purposes, but the savings in gas and reagents also cannot be neglected. In addition, there are economies in apparatus and bench-space. The greatest advantages are, however, the high degree of accuracy usually obtainable, and the fact that the practice of micro-technique is one of the most valuable forms of laboratory training. If this technique is acquired at an early stage it will always be retained and used, for few chemists ever wish to return to the clumsier macro-methods.

In general the methods of working are the same as in macro-work, *e.g.* precipitation, filtration, evaporation, etc., except that one uses a few milligrams of material (or cubic centimetres of solution), and in some cases only drops.

The metals may be separated first into groups and then from one another by the usual reactions described in the succeeding pages, but in many cases there are selective tests

which enable one particular metal or acid radical to be distinguished in the presence of others without preliminary separation. Although these "short-cut" methods are exceedingly useful in practice, especially as confirmatory tests, they have not the educational value of the separations, and the student is urged not to neglect the latter. A thorough knowledge of these and the principles on which they depend is essential to every chemist.

Apparatus.—The apparatus is very simple. Thick-walled glass tubing (diameter 1 cm.) is drawn out to form small test-tubes, pipettes, etc., and a few microscope slides, micro-crucibles (holding about 1 c.c.) and watch-glasses are also required. White and black tiles with depressions, and filter papers are useful for spot tests, and dropping-bottles are used for reagents. A micro-bunsen or a hard-glass tube drawn out to a jet is desirable.

In certain so-called "crystal tests" one depends on the formation of crystals of characteristic shape, and in such cases a microscope or a good lens is essential. A good microscope is unnecessary, and indeed not advisable, because it may be damaged by contact with reagents or vapours, or may undergo other forms of rough usage.

Methods.—The match, film, flame, and bead tests described on pages 6 to 10 are really micro-tests, and others are described below and in connection with organic analysis (p. 241).

Ignition and fusion are carried out in the micro-crucible or on a piece of platinum foil; the substance may be heated with a bead of fusion-mixture in a loop on a platinum wire.

Evaporation in a watch-glass on a hot-plate is very convenient, or drops may be evaporated on glass slides held high up over the flame of the micro-burner.

Solubility.—A speck of material is moved into a drop of solvent placed beside it by means of a thin glass rod drawn out to a point, on the end of which is a round knob. Careful

observation will detect any tendency to dissolve, and if this is small a portion of the drop may be evaporated, and any solid residue noted. Evolution of gas (*e.g.* from acids and carbonates) is easily visible under such conditions, especially if a lens is used.

The borax and microcosmic bead tests (p. 10) are very useful as means of obtaining solutions of the less soluble salts for micro-tests. The substance is heated in the bead in the usual way, and the bead is dissolved in acid on a watch-glass. The solution is evaporated, and the residue is ready for the micro-reaction.

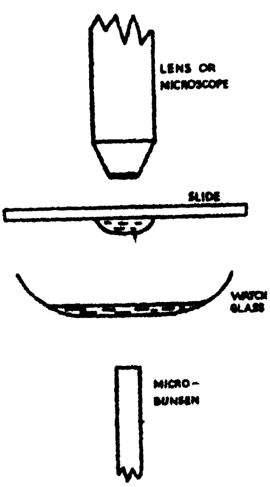


FIG. 5.

Gases and vapours may be tested by generating them on a watch-glass and allowing them to come into contact with a drop of reagent suspended from the underside of a microscope slide (Fig. 5). The formation of a precipitate (*e.g.* from carbon dioxide and lime water) may be observed from above through a lens.

Micro-generators for gases are available (*e.g.* for hydrogen sulphide), but a fine glass jet on an ordinary generator is usually quite satisfactory.

Precipitation may take place in the small test-tubes, or two drops may be brought just into contact on a slide by means of a thin glass rod (Fig. 6) which is drawn out to a point with a knob on the end. The slide should first be held in the flame to remove any grease which may prevent the drops from following the rod. It is a good plan not to allow the drops to mix at once, but to observe the junction of them carefully, as in this way the redissolution of the precipitate in an excess of reagent may be seen. With white precipitates the slide should be held over a black tile, and over a white tile with

coloured precipitates ; the slide may be gently heated or other reagents may be added.

Filtration.—With 2 to 10 mgrms. of solid or solution the Emich filter stick, which is about 4 cm. in length, is used. The lower and wider end is made of sintered glass or porcelain,

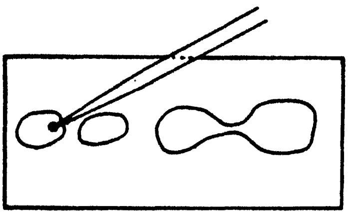


FIG. 6.

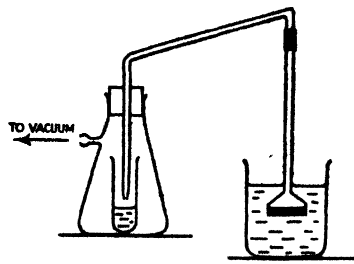


FIG. 7.

and is inserted in the liquid, suction being applied to the test-tube as shown in Fig. 7, so that the liquid is drawn over, while the solid remains on the end of the filter stick. In certain cases the centrifuge provides an excellent method of separating solids from liquids and even of washing the former.

With drops, a piece of glass tubing (diameter 1 mm.) with a clean-cut end, is pressed on a small square of filter paper, the edge of which is moved carefully to the edge of the drop. The liquid can then be drawn into the tube, leaving the solid on the edge of the paper (Fig. 8).



FIG. 8.

Spot- or Drop-Tests.—As mentioned above, these are most conveniently carried out on spotting-tiles or on filter paper. In the former case the procedure outlined under precipitation is applied. In the latter, a drop of reagent is usually placed on a piece of best quality filter paper, and this is allowed to

dry in a warm place before the test-solution or other reagents are added.

Microscope Tests usually involve the formation of crystals of characteristic colours or shapes, and they are therefore best produced from solid materials and observed under the microscope. Solutions are therefore evaporated, and a speck of the solid is brought into a drop of reagent as described under Solubility (above).

The low-power of the microscope (*e.g.* a magnification of 100 to 200) should be used, as it gives a larger field of vision. The objective should be racked down as near the drop as possible *before* the eye is applied to the eyepiece, and then racked up when the eye is in position, to get the correct focus. This minimises the possibility of damaging the objective by immersion in the reagent, especially as cover-slips are seldom used. Slides with depressions are very useful for this work.

All the tests and separations described in the following pages can and should be carried out by micro-methods, once the student has become familiar with them, but in addition special drop and microscope (crystal) reactions are given for each metal, and in many cases these are selective in the presence of mixtures. Although the drop reactions will be found very simple and convenient, the crystal tests require a little practice. Once they are mastered, however, like the drop reactions, they will be found particularly useful, especially for confirmatory tests in the group separations (see pp. 214, etc.). It is advisable always to draw sketches of the crystals observed, as in this way their essential features are impressed on the memory. The sensitiveness of micro-reactions is expressed in terms of the quantity γ, where $1\gamma = 0{\cdot}001$ milligram (one-millionth of a gram).

Further details of micro-technique are given in the introduction to "Organic Analysis" (p. 241).

CHAPTER III.

DIVISION OF THE METALS INTO GROUPS.

In analytical chemistry the metals are divided into groups, according to their behaviour with certain reagents. For convenience of arrangement, it is usual to number these groups i., ii., iii., etc. ; but this arrangement has the disadvantage of loss of individuality. The student is apt to talk in a vague manner of group i., group ii., etc., often forgetting the principles which underlie such an arrangement. In this book, therefore, the groups are not numbered, but are designated by the name of a characteristic element. It is not possible within the scope of this book to give complete analytical tables for the separations of the rarer metals, nor, indeed, to set out the reactions of all of them. In fact, owing to the similarity of the reactions of some of them, analytical separations are often extremely difficult. Many of the elements are exceedingly rare, and are therefore much too expensive to procure for ordinary analytical practice. The reactions of some of the more frequently used or occurring of these elements are, however, given in the groups to which they belong. The order of arrangement is as follows :—

Silver Group (Group reagent: *hydrochloric acid*).—This group consists of **silver, lead,** and **mercurous mercury,** the chlorides of which are insoluble in water (lead chloride is soluble in hot water). Thallium and Tungsten are precipitated with the metals of the silver group, the first as **thallous chloride** $TlCl$, and the second as **tungstic acid,** H_2WO_4. The chlorides are precipitated by the addition of the group reagent, **hydrochloric acid,** to solutions of their salts.

Copper Group (Group reagent: *hydrochloric acid* and *hydrogen sulphide*).—This group contains **mercuric mercury, lead, copper, bismuth,** and **cadmium,** the sulphides of which are all insoluble in water and in dilute hydrochloric acid. They are, therefore, precipitated in acid solution by the addition of a solution of hydrogen sulphide or when a stream of the gas is passed through solutions of the salts of these metals. They are *insoluble* in alkali sulphides and in caustic alkalis.

Arsenic Group.—The metals of this group, **arsenic, antimony, tin, gold,** and **platinum,** are also precipitated as sulphides by hydrogen sulphide in acid solution. Their sulphides differ, however, from those of the copper group in being *soluble* in alkali sulphides and in caustic alkalis.

Ruthenium, Ru_2S_2; Rhodium, Rh_2S_3; Palladium, PdS; Osmium, OsS; Iridium, Ir_2S_3; Molybdenum, MoS_3; and the Metalloids, Selenium (ppt. as Se), and Tellurium, TeS_2. The sulphides Ir_2S_3, TeS_2, MoS_3, and Selenium as metalloid are soluble in ammonium sulphide.

Iron Group (Group reagents: *ammonium chloride,* followed by *ammonium hydroxide, and hydrogen sulphide* [*ammonium sulphide*]).—The metals **iron, nickel, cobalt, zinc, manganese, chromium, aluminium,** and **cerium** are either precipitated by hydrogen sulphide in ammoniacal solution, or are, on the addition of ammonium hydroxide thrown out as hydroxides. For example, when their solutions are made alkaline with ammonium hydroxide in presence of ammonium chloride, **iron, aluminium, chromium,** and **cerium** are precipitated as hydroxides. This fact is used to separate these metals from the other metals of the group.

The addition of ammonium chloride before adding **ammonium hydroxide** is to prevent precipitation of **manganese, cobalt, nickel, zinc,** and **magnesium hydroxides.** (See p. 217.)

Beryllium (Glucinum), $Be(OH)_2$; Cerium, $Ce(OH)_3$; Scandium, $Sc(OH)_3$; Yttrium, $Y(OH)_3$; Ytterbium, $Yt(OH)_3$; Lanthanum, $La(OH)_3$; Thorium, $Th(OH)_3$; Zirconium,

$Zr(OH)_4$; Titanium, H_2TiO_3; Tantalum, H_3TaO_4; Niobium (Columbium), H_3NbO_4; Uranium, $(UO_2)S$; Indium, InS; Vanadium (not ppt. as sulphide, see reactions, p. 111). The elements to and including Zirconium form basic hydroxides. Titanium, Tantalum, and Niobium form acidic hydrated oxides, while Uranium and Indium form sulphides.

Barium Group (Group reagent: *ammonium carbonate*).—The metals **barium, strontium,** and **calcium** all form carbonates which are insoluble in water, and are precipitated from alkaline solution by the addition of **ammonium carbonate.**

Sodium Group.—This group includes **magnesium, potassium, sodium, lithium, rubidium, cæsium,** and **ammonium.** They are not precipitated by any of the group reagents already mentioned. There is, in fact, no common reagent known which will precipitate them all. Furthermore, although ammonium is included in this group, it is never tested for at this stage, but in the original substance, because it is necessary to add soluble ammonium salts in the separation of the preceding groups.

Reactions of the Metals.—**1.** Only small quantities of the solution of the metallic salt should be taken, and the solution should not be a strong one. Most of the reactions, being very delicate, are better shown in dilute solutions. In this connection it is an excellent plan to attempt, so far as possible, to keep qualitative analysis as near quantitative as possible. It is not necessary actually to weigh the precipitates, but only to make a mental note or guess of the quantity of material originally taken (say 0·1 grm.) and of each of the precipitates as it is produced. If this habit is acquired at the start a fairly high degree of accuracy will be obtainable which is of great help in practice, where the qualitative examination is frequently merely a preliminary to a full quantitative analysis.

2. Strength of Reagents.—It is recommended that all solutions employed should be of known strength, because *e.g.* if a given volume of an alkali is added, it can be neutralised if

necessary by the addition of the correct volume of an acid solution. This will also help to keep the reactions quantitative. Four times normal (4N.) is a very convenient strength. For further particulars, see p. 360.

3. When testing the solubility of a precipitate, filter it from the solution in which it is suspended. The method of adding a solvent without first filtering is slovenly, and often leads to error.

4. The reactions of the metals should not be hurried as if they were of no importance. The more carefully the student has worked through the reactions, the better will he be able to understand the theoretical and practical importance of the analytical separations.

5. Careful notes should be taken, and an experiment should **never** be attempted without first carefully reading through the directions given. With the crystal tests sketches should be made of the crystal forms observed, and retained for reference.

THE SILVER GROUP.

Silver.

Silver is readily soluble in moderately strong nitric acid, with evolution of nitric oxide.

$$3Ag + 4HNO_3 = 3AgNO_3 + NO + 2H_2O$$

It also dissolves in hot strong sulphuric acid, sulphur dioxide being evolved.

$$2Ag + 2H_2SO_4 = Ag_2SO_4 + SO_2 + 2H_2O$$

Dry Reactions.—*Blowpipe Test.*—When heated on charcoal with fusion mixture (see p. 369), silver compounds yield a bright metallic bead of silver.

Match Test.—Beads of silver obtained.

Reactions in Solution.—Use a solution of silver nitrate.

* **1.**† **Sodium or potassium hydroxide** gives a dark brown,

† The most important reactions are marked thus *. Dry reactions, although not marked with an asterisk, should never be neglected.

amorphous precipitate of **silver monoxide**. When freshly precipitated, this substance behaves as if it is **silver hydroxide**.

$$AgNO_3 + KOH = AgOH + KNO_3$$
$$2AgOH = Ag_2O + H_2O$$

It is readily soluble in ammonia, with the formation of silver ammonium hydroxide,—the silver replacing one of the hydrogen atoms of the NH_4 group, and thus forming a complex cation. The dry oxide is completely decomposed into metallic silver and oxygen when heated to about 300°.

$$Ag_2O + 2NH_4OH = 2AgNH_3OH + H_2O$$

2. Ammonium hydroxide produces the same precipitate which immediately dissolves in excess. Therefore if the ammonium hydroxide is incautiously added, the precipitate is not observable.

***3. Hydrochloric acid,** or soluble chlorides, form a white, curdy precipitate of **silver chloride**, which darkens on exposure to light.

$$AgNO_3 + HCl = AgCl + HNO_3$$

It is readily soluble in ammonium hydroxide and in potassium cyanide. It is also partially soluble in excess of strong hydrochloric acid or of alkali chlorides, and in concentrated solutions of magnesium chloride. Nitric acid reprecipitates it from these solutions.

$$AgCl + NH_3 = AgNH_3Cl$$
$$AgCl + 2KCN = KAg(CN)_2 + KCl$$

***4. Potassium chromate** in neutral solutions produces a brick-red precipitate of **silver chromate**, insoluble in cold acetic acid, but readily soluble in mineral acids ; so that no precipitation takes place in presence of mineral acids.

$$2AgNO_3 + K_2CrO_4 = Ag_2CrO_4 + 2KNO_3$$

***5. Hydrogen sulphide** gives a black precipitate of **silver sulphide**, insoluble in dilute acids, soluble in hot **nitric acid**.

$$2AgNO_3 + H_2S = Ag_2S + 2HNO_3$$

6. Metallic zinc precipitates metallic silver from its solutions. Even silver chloride is decomposed if it is suspended in dilute sulphuric acid, and zinc added. The zinc and the silver chloride must be in intimate contact.

7. Drop Reaction.—Dissolve a little of the silver chloride in a drop of ammonia, and spot it on a filter paper. Then add to the spot, 1 drop of a 0·03 per cent. solution of *p*-dimethyl-amino benzal rhodanine in acetone, and 1 drop of *N* nitric acid. A red-brown colour indicates silver. This test may be applied to a precipitate containing the other metals of the silver group by adding 2 drops of a 5 per cent. potassium cyanide solution, filtering and testing the filtrate.

8. Crystal Test.—A little solid hexamethylene tetramine is added to a drop of the solution. Colourless monoclinic plates or needles are produced, the reaction being stimulated by addition of a drop of potassium iodide.

$$2AgCl + Zn = 2Ag + ZnCl_2$$

Lead.

Lead is insoluble in dilute sulphuric and hydrochloric acids. It dissolves in nitric acid with evolution of nitric oxide.

$$3Pb + 8HNO_3 = 3Pb(NO_3)_2 + 2NO + 4H_2O$$

With concentrated nitric acid a white crystalline residue of lead nitrate is obtained, which dissolves on addition of water.

Dry Reactions.—*Blowpipe Test.*—When heated on charcoal lead compounds are reduced to the metal, the reduction being more complete if the lead compound is mixed with fusion-mixture. The bead so obtained is soft, and can be easily cut with a penknife. When drawn across a sheet of white paper it leaves a black mark. A yellow incrustation of PbO is, at the same time, formed on the charcoal.

Match Test.—Malleable beads of metallic lead are obtained, having the properties already described.

Film Test.—See table, p. 198.

Flame Test.—Lead compounds impart a pale blue appearance to the flame of a Bunsen burner.

Reactions in Solution.—Use a solution of **lead acetate** or **nitrate.**

*1. **Hydrochloric acid** produces in cold solutions a white precipitate of **lead chloride,** which is soluble in boiling water, and separates out again, on cooling, in brilliant needles. It is insoluble in ammonium hydroxide.

$$Pb(NO_3)_2 + 2HCl = PbCl_2 + 2HNO_3$$

*2. **Hydrogen sulphide** gives a black precipitate of **lead sulphide,** soluble in dilute nitric acid. On boiling with strong nitric acid it is converted into **lead sulphate.**

$$Pb(NO_3)_2 + H_2S = PbS + 2HNO_3$$
$$3PbS + 8HNO_3 = 3PbSO_4 + 8NO + 4H_2O$$

When hydrogen sulphide is passed into lead solutions containing much hydrochloric acid the precipitate is first brownish-red, and consists of $PbCl_2 . PbS$.

3. **Sulphuric acid** throws down a white precipitate of **lead sulphate,** soluble in ammonium acetate, ammonium tartrate, and concentrated sodium or potassium hydroxide (distinction from barium sulphate).

$$Pb(NO_3)_2 + H_2SO_4 = PbSO_4 + 2HNO_3$$

Lead sulphate is slightly soluble in water, but is almost insoluble in water containing an equal bulk of alcohol. The solubility in ammonium acetate is probably due to the formation of a molecule of lead acetate and one of ammonium plumbisulphate thus—

$$2PbSO_4 + 2CH_3COONH_4 = Pb\begin{cases} O.SO_2.ONH_4 \\ O.SO_2.ONH_4 \end{cases} + (CH_3.COO)_2Pb.$$

Lead sulphate is again precipitated from this solution by addition of sulphuric acid, or on dilution with water.

Sodium or **potassium hydroxide** produces a white precipitate of **lead hydroxide.**

$$Pb(NO_3)_2 + 2KOH = Pb(OH)_2 + 2KNO_3$$

It is soluble in excess of caustic alkali, with formation of a complex anion, lead plumbite, thus—

$$Pb(OH)_2 + 2KOH = Pb(OK)_2 + 2H_2O$$

4. Potassium iodide gives a yellow precipitate of **lead iodide,** soluble in hot water. On cooling, the lead iodide, separates out in beautiful golden-yellow plates.

$$Pb(NO_3)_2 + 2KI = PbI_2 + 2KNO_3$$

***5. Potassium chromate** produces a yellow precipitate of **lead chromate** (" chrome yellow "), soluble in nitric acid.

$$Pb(NO_3)_2 + K_2CrO_4 = PbCrO_4 + 2KNO_3$$

If the lead chromate is warmed with a little sodium hydroxide, it is converted into basic **lead chromate** (" chrome red ") $PbCrO_4, PbO$, soluble in excess to give a yellow solution.

6. Drop Reaction.—Spot a drop of the solution on a filter-paper, and add a drop each of 1 per cent. pyridine in water and of a mixture of 0·1 per cent. gallocyanine and sodium bicarbonate. Lead gives a deep violet spot (sensitiveness 6γ). Other metals (*e.g.* silver and copper) should first be removed by washing the spot with a few drops of sulphuric acid followed by alcohol, and excess of reagent is removed similarly with pyridine.

7. Crystal Test.—The reaction described for potassium (§ 6, p. 129) may be used for lead if potassium acetate is substituted for lead acetate in the preparation of the reagent (p. 371).

Mercury.

This metal differs from all others in being liquid at ordinary temperatures (m.p. — 38·8°); it boils at 357·2°. It is insoluble in hydrochloric acid, but soluble in hot sulphuric and nitric acids.

Mercury forms two series of salts: **mercurous compounds** such as Hg_2Cl_2, $Hg_2(NO_3)_2$, which are derived from **mercurous oxide,** Hg_2O, and **mercuric compounds** such as $HgCl_2$, $Hg(NO_3)_2$, derived from **mercuric oxide,** HgO.

In preparing mercur*ous* compounds by the action of acids on mercury, it is necessary to have an excess of the metal present, and when kept in solution a little metallic mercury should always be placed in the bottle (reaction *a*). If the acid is in excess, mercur*ic* compounds are formed (reaction *b*).

$$(a)\ 6Hg + 8HNO_3 = 3Hg_2(NO_3)_2 + 2NO + 4H_2O$$
$$(b)\ 3Hg + 8HNO_3 = 3Hg(NO_3)_2 + 2NO + 4H_2O$$

General Reactions for Mercury Compounds.—1. When heated in a dry tube most mercury compounds sublime, condensing unchanged on the cool portions of the tube. Some however, such as the oxide, nitrate, and chromate are decomposed, *e.g.*—

$$2Hg(NO_3)_2 = 2HgO + 4NO_2 + O_2$$
$$2HgO \rightleftharpoons 2Hg + O_2$$

2. When mixed with fusion-mixture or, better, with soda lime, and heated in a dry tube, mercury compounds are reduced to metallic mercury, which is deposited as a grey mirror on the cool part of the tube.

3. *Film Test.*—See table, p. 198.

4. A clean piece of copper placed in neutral or slightly acid solutions becomes coated with a film of mercury; on gently rubbing with a piece of filter paper, the surface assumes the appearance of polished silver. When the piece of "silvered" (or "amalgamated") copper is dried, first by filter paper and then by gently warming in the Bunsen flame, and is heated in a dry test-tube the mercury sublimes, condensing on the upper portions of the tube.

Mercurous Compounds.

Use a solution of **mercurous nitrate.**

***1. Hydrochloric acid** gives a heavy white precipitate of **mercurous chloride** (calomel), insoluble in hot water and in acids, but soluble in aqua regia ; and, in bromine or chlorine water, which converts it into a soluble mercuric salt.

$$Hg_2(NO_3)_2 + 2HCl = Hg_2Cl_2 + 2HNO_3$$

It is turned black by addition of ammonium hydroxide, mercuro-ammonium chloride being produced.

$$2HgCl + 2NH_3 = Hg_2NH_2Cl + NH_4Cl$$

All mercurous compounds are turned black by alkaline hydroxides. Sodium or potassium hydroxide precipitates black **mercurous oxide.**

$$Hg_2(NO_3)_2 + 2NaOH = Hg_2O + 2NaNO_3 + H_2O.$$

***2. Hydrogen sulphide** produces a black precipitate of **mercuric sulphide,** *not of mercur*ous *sulphide.* The precipitate also contains finely-divided metallic mercury.

$$Hg_2(NO_3)_2 + H_2S = HgS + Hg + 2HNO_3$$

On warming with nitric acid the mercury alone is dissolved, mercuric sulphide being soluble only in aqua regia. See p. 47.

***3. Stannous chloride** gives a white precipitate of **mercurous chloride,** which on warming with excess of stannous chloride turns grey, owing to separation of mercury. On pouring off the supernatant liquid and warming with a little strong hydrochloric acid, mercury aggregates into a globule. When an excess of the stannous chloride is added in the first place, an immediate grey precipitate is produced, the reaction passing directly to the second stage.

$$Hg_2(NO_3)_2 + SnCl_2 = Hg_2Cl_2 + Sn(NO_3)_2$$
$$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4$$

4. Potassium iodide precipitates from solutions, which are not too strongly acid, a bright yellow or yellow-green precipitate of **mercurous iodide.**

$$Hg_2(NO_3)_2 + 2KI = Hg_2I_2 + 2KNO_3$$

With an excess of potassium iodide, in which mercurous iodide is soluble, a slight grey precipitate of mercury is produced on boiling.

$$Hg_2I_2 + 2KI = K_2HgI_4 + Hg$$

5. Drop Reaction.—There is no reliable selective spot test for mercurous ions, but the reaction described under mercuric compounds may be used.

6. Crystal Test.—A drop of strong hydrochloric acid is added to the solution, and the fine needles of mercurous chloride may be observed at the junction of the drops under the microscope.

Tungsten.

Tungsten minerals are fairly widely distributed, but are by no means plentiful. The metal is very hard, and has somewhat the appearance of iron.

Tungsten forms two oxides, tungstous oxide, WO_2, a brown powder obtained by heating tungstic oxide in a stream of hydrogen—

$$WO_3 + H_2 = WO_2 + H_2O$$

Tungstic oxide, WO_3, is an acid anhydride which is produced by ignition of tungstic acid—

$$H_2WO_4 = WO_3 + H_2O$$

It is a bright yellow powder insoluble in dilute acids, readily soluble in warm alkali hydroxides. ✓

Dry Reactions.—1. *Microcosmic Bead.*—Colourless in the oxiding flame, bright blue in reducing flame, the addition of ferrous sulphate causes it to become blood-red.

Reactions in Solution.—Use a solution of sodium tungstate.

1. Mineral Acids give in the cold a white, more or less gelatinous precipitate of tungstic acid H_2WO_4, H_2O. On

boiling, or when precipitated from boiling solutions, the yellow anhydrous acid is produced. In presence of phosphates precipitation is not complete, and it is prevented by tartaric acid.

$$Na_2WO_4 + 2HCl = H_2WO_4 + 2NaCl$$

When hydrochloric acid is added drop by drop to a boiling solution of a tungstate no precipitate is formed, but after long continued boiling the yellow tungstic acid is precipitated (distinction from molybdenum).

2. **Ammonium sulphide** produces no precipitate, but if the solution is afterwards acidified a brown precipitate of WS_3 is produced, which can be redissolved in ammonium sulphide.

3. **Mercurous nitrate** gives a white precipitate of mercurous tungstate from neutral solutions, the precipitate rapidly turns yellow.

$$Na_2WO_4 + Hg_2(NO_3)_2 = Hg_2WO_4 + 2NaNO_3$$

On ignition mercury is driven off and WO_3 remains; this is used to determine tungsten quantitatively.

4. **Stannous chloride** first produces a yellow coloration or precipitate, which, on the addition of hydrochloric acid and warming, changes to a brilliant blue coloration or precipitate. This reaction is extremely delicate.

$$WO_3 + SnCl_2 + 2HCl = WO_2 + SnCl_4 + H_2O$$

Thallium.

Forms Thallous and Thallic Compounds Tl_2O and Tl_2O_3.

Thallous Compounds.

Colourless and generally soluble in water. The sulphide, bromide, chloride, iodide, and chromate are insoluble in water. Thallous oxide is soluble in water to which it imparts an alkaline reaction, and the solution absorbs CO_2 from the air.

Dry Reactions.—*Flame Test*—Thallium salts colour the flame of the Bunsen burner a brilliant green. The spectrum shows a brilliant green line.

Film Test.—Metal Film : Blackish-brown, soluble in 20 per cent. HNO_3. Oxide Film : colourless. Ammonium sulphide : reddish-brown with black edges. Iodide : light yellow, intense yellow when breathed upon.

1. **Hydrogen sulphide** gives no precipitate in solutions containing mineral acid. The precipitation from neutral solutions (black Tl_2S) is also incomplete.

2. **Ammonium sulphide** gives a black precipitate of thallous sulphide, Tl_2S. Readily soluble in mineral acids, but insoluble in acetic acid. On standing in the air it readily oxidises to thallous sulphate.

$$Tl_2SO_4 + (NH_4)_2S = Tl_2S + (NH_4)_2SO_4$$

3. **Hydrochloric acid** produces a heavy white precipitate of **thallous chloride,** slightly soluble in water but much less so in water containing hydrochloric acid.

$$Tl_2SO_4 + 2HCl = 2TlCl + H_2SO_4$$

4. **Potassium iodide** forms a light yellow precipitate of the iodide—the reaction is extremely delicate (**Micro-Reaction**).

$$Tl_2SO_4 + 2KI = 2TlI + K_2SO_4$$

5. **Potassium chromate** gives a yellow precipitate of thallous chromate insoluble in cold mineral acids.

$$Tl_2SO_4 + K_2CrO_4 = Tl_2CrO_4 + K_2SO_4$$

6. **Hydroplatinic acid** produces a light yellow precipitate of **thallium chloroplatinate,** which is extremely insoluble.

$$Tl_2SO_4 + H_2PtCl_6 = Tl_2PtCl_6 + H_2SO_4$$

7. **Sodium cobaltinitrite** gives a scarlet precipitate of thallous cobaltinitrite.

$$3Tl_2SO_4 + 2Na_3Co(NO_2)_6 = 2Tl_3[Co(NO_2)_6] + 3Na_2SO_4$$

Thallic Compounds.

Thallic chloride can be prepared by the action of chlorine water on thallous chloride.

1. **Alkali hydroxides** give a brown precipitate of thallic hydroxide, insoluble in excess of alkali and sparingly soluble in acids.

$$TlCl_3 + 3NaOH = Tl(OH)_3 + 3NaCl$$

2. **Potassium iodide** produces a precipitate of thallous iodide, and at the same time iodine is liberated.

$$TlCl_3 + 3KI = TlI + I_2 + 3KCl$$

3. **Crystal Test.**—The triple nitrite reagent (p. 371) gives similar crystals as with potassium (§ 6, p. 129).

Analysis of the Metals of the Silver Group.—The separation of the metals of the silver group depends on the behaviour of the chlorides with boiling water and with ammonium hydroxide.

Lead chloride is soluble in boiling water, **silver and mercurous chlorides** are insoluble.

Silver chloride is soluble in **ammonium hydroxide, lead chloride** is insoluble, and **mercurous chloride** is turned into a black insoluble compound (see p. 41).

In order to analyse the solution, add dilute hydrochloric acid until no further precipitate is produced, allow to settle, pour off the excess of solution, and add water.

I. Boil the mixture and filter hot, washing the residue on the filter paper several times with hot water.

The solution contains lead chloride which crystallises out on cooling. The presence of lead may be further confirmed by adding potassium dichromate to the hot solution, when a yellow precipitate of **lead chromate** will be produced.

The residue on the filter paper is treated with ammonium hydroxide, which dissolves out the silver chloride, the mercurous chloride being turned black.

The presence of silver chloride in the filtrate is demonstrated by acidifying the ammoniacal solution with nitric acid,

when it is reprecipitated. The black residue of **mercurous ammonium chloride** may be dissolved in aqua regia, the solution evaporated to a small bulk, diluted with excess of water, and a piece of copper foil placed in it, when the copper will be coated with a grey film of mercury, which becomes bright when gently rubbed.

II. When there are very small quantities of silver present with considerable amounts of a mercurous salt, it is often difficult, if not impossible, to separate the silver by dissolution in ammonia as described above. Therefore the following method of separation is better :—

Separate the lead chloride by boiling water in exactly the same way as above described. Now transfer the filtered and washed residue to a test-tube, cover with water and add small quantities of bromine water, warming between each addition, until on allowing the precipitate to settle, the solution has a permanent light brown colour. The **residue** is a mixture of silver chloride and bromide, which after filtering and washing, may be dissolved in a little strong warm ammonia, from which it can again be precipitated by addition of nitric acid.

The *solution* contains mercur*ic* chloride and bromide. Boil off the excess of bromine, add a few drops of nitric acid and a small piece of clean copper foil, which will become coated with a film of mercury.

CHAPTER IV.

THE COPPER GROUP.

Mercuric Compounds.

USE a solution of **mercuric chloride.**

***1. Hydrogen sulphide,** when added in very small quantities to a solution of a mercuric salt, throws down a white precipitate which is a double compound of the mercuric salt taken, and of mercuric sulphide (*e.g.* $HgCl_2$, $2HgS$): on adding further quantities of hydrogen sulphide, the precipitate becomes yellow, then reddish-brown, and finally black, the black precipitate consisting entirely of **mercuric sulphide.**

$$(a)\ 3HgCl_2 + 2H_2S = HgCl_2 . 2HgS + 4HCl$$
$$(b)\ HgCl_2, 2HgS + H_2S = 3HgS + 2HCl$$

Mercuric sulphide is insoluble in nitric or hydrochloric acid, but it is readily soluble in aqua regia. On boiling for some time with nitric acid, it is converted into the white salt $Hg(NO_3)_2$, HgS. It is also readily soluble in a strong solution of sodium sulphide, especially if this contains polysulphides or free alkali.

***2. Sodium** or **potassium hydroxide** gives a yellow precipitate of **mercuric oxide.**

$$2NaOH + HgCl_2 = HgO + 2NaCl + H_2O$$

When added in very small quantities a brownish-red basic salt is at first produced. This last reaction is shown best when hot solutions are used or if barium or calcium hydroxide is taken.

3. Ammonium hydroxide produces a white precipitate of **mercuro-ammonium chloride.**

$$HgCl_2 + 2NH_4OH = NH_2HgCl + NH_4Cl + 2H_2O$$

4. Potassium iodide gives a beautiful red precipitate of **mercuric iodide.**

$$HgCl_2 + 2KI = HgI_2 + 2KCl$$

The precipitate, when first formed, comes down yellow, but rapidly changes to red. It is soluble in excess of either potassium iodide or mercuric chloride to produce a colourless solution. In the former case it forms a complex salt the cation of which is potassium, the mercury being in the anion; therefore from this solution mercury is not precipitated by most of the ordinary reagents. It is, however, precipitated by hydrogen sulphide. Nessler's reagent is an alkaline solution of this salt (p. 132).

$$HgI_2 + 2KI = K_2HgI_4$$

***5. Stannous chloride** precipitates **mercurous chloride,** which, if an excess of the reagent has been added, rapidly becomes reduced to grey metallic mercury. On boiling this with a little concentrated hydrochloric acid, the mercury separates as a globule.

$$(a)\ 2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$$
$$(b)\ Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4$$

6. Hypophosphorous acid precipitates metallic mercury from its salts on warming. This is used as a quantitative method for the determination of mercury.

$$2HgCl_2 + H_3PO_2 + 2H_2O = H_3PO_4 + 2Hg + 4HCl$$

7. Drop Reaction—Moisten a filter paper with a drop of a fresh 1 per cent. solution of diphenylcarbazide in alcohol, and add a drop of the test solution which should be about 0·2 *N* with respect to nitric acid. A violet or blue spot results with 1γ of mercuric ions. The reaction is also used for cadmium, magnesium and chromium.

8. Crystal Test.—The mercuric thiocyanate test for cobalt (§ 8, p. 106) may be applied to mercuric ions by using a mixture of cobalt acetate and a slight excess of ammonium thiocyanate in the presence of acetic acid.

Bismuth.

Bismuth is readily soluble in nitric acid, nitric oxide being evolved.

$$2Bi + 8HNO_3 = 2Bi(NO_3)_3 + 2NO + 4H_2O$$

It is insoluble in dilute sulphuric acid, and only slightly soluble in hydrochloric acid. Bismuth forms many alloys, most of which can be dissolved in nitric acid for the purposes of analysis. The trivalent bismuth ion is very weakly basic, therefore its salts are hydrolysed by water with the formation of almost insoluble hydroxy salts.

Dry Reactions.—1. *Flame Test.*—Bismuth compounds impart a pale blue colour to the flame of the Bunsen burner.

2. *Dry Tube Test.*—When heated in a dry test-tube, bismuth salts are decomposed into the oxide, which is orange-red while hot, and becomes yellow on cooling.

3. *Blowpipe Test.*—When heated on charcoal with fusion mixture, a brittle metallic bead is obtained, an orange-red incrustation, which becomes light yellow on cooling, being formed on the charcoal at the same time.

4. *Match Test.*—A brittle bead of metallic bismuth is obtained.

5. *Film Test.*—See table, p. 198.

Reactions in Solution.—Use a solution of **bismuth nitrate** or **chloride.**

*1. **Hydrogen Sulphide** gives a dark brown, almost black, precipitate of **bismuth sulphide,** readily soluble in warm nitric acid.

$$2Bi(NO_3)_3 + 3H_2S = Bi_2S_3 + 6HNO_3$$

*2. **Alkali hydroxides** and **ammonium hydroxide** produce a white precipitate of **bismuth hydroxide,** $BiO(OH)$ or $Bi(OH)_3$, *insoluble* in excess of the reagent (distinction from cadmium, the hydroxide of which is soluble in ammonium hydroxide).

*3. **Water,** added to a moderately acid solution of a bismuth salt, forms a white precipitate of an oxy-salt. If the

solution of the bismuth salt is very dilute, only a cloudy appearance is produced.

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$
$$Bi(NO_3)_3 + H_2O \rightleftharpoons 2HNO_3 + BiO(NO_3)$$

In order to show this reaction to advantage, it is best to pour the bismuth solution into about 500 c.c. of water, to which some ammonium chloride has been added.

The oxy-salts of bismuth are *insoluble* in tartaric acid (distinction from antimony). They are also *insoluble* in alkali hydroxides (distinction from tin). The formation of oxy-salts is due to hydrolysis, the bismuth ion being very weakly basic.

The formation of the oxy-salts may be expressed as a reversible reaction, because excess of acid causes the formation of the normal salt. This is an excellent example of the Law of Mass Action (p. 23).

It should be noted that in the case of bismuth nitrate a further excess of water results in the formation of crystalline *bismuth subnitrate* of the Pharmacopœia.

$$2BiO(NO_3) + H_2O \rightleftharpoons HNO_3 + O : BiO . Bi\begin{cases} OH \\ NO_3 \end{cases}$$

√ 4. **Potassium iodide** gives a chocolate-coloured precipitate of bismuth iodide,

$$Bi(NO_3)_3 + 3KI = BiI_3 + 3KNO_3,$$

soluble in excess to produce a deep yellow solution.

$$BiI_3 + KI = KBiI_4.$$

Addition of water reprecipitates the bismuth iodide; excess converts it into orange-coloured BiOI.

5. **Alkali stannites.**—Take a few drops of stannous chloride and add caustic alkali until the white precipitate at first produced just dissolves. To this solution, which must be cold, add the bismuth solution and shake. A black precipitate of bismuth is at once formed.

$$3SnCl_2 + 2BiCl_3 + 18NaOH = 2Bi + 3SnO(ONa)_2 + 12NaCl + 9H_2O$$

6. Drop Reaction.—A drop of a mixture of a 1 per cent. solution of cinchonine in very dilute nitric acid and of 2 per cent. potassium iodide is mixed (*e.g.* on a filter paper) with the acid solution of bismuth, when an orange-red colour appears (sensitiveness 0·14 γ). Lead gives a yellow colour and copper brown (due to iodine).

7. Crystal Test.—To a solution of the bismuth salt in strong hydrochloric acid is added a drop of sodium iodide solution and a crystal of cæsium chloride. Red six-sided crystals are produced (Cs_2BiCl_5). Sensitiveness 0·2 γ.

Copper.

Copper is readily soluble in nitric acid, with evolution of nitric oxide.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$$

It also dissolves slowly in dilute sulphuric acid ; *readily* in boiling concentrated acid, with evolution of sulphur dioxide. The equation usually given for this reaction is incorrect, it being assumed that SO_2, $CuSO_4$, and H_2O alone are formed, whereas only a portion of the copper is converted into sulphate, considerable quantities of sulphide being also produced.

$$5Cu + 4H_2SO_4 = 3CuSO_4 + Cu_2S + 4H_2O$$

Copper is least soluble in hydrochloric acid. Copper forms many important alloys, such as **bronze** (copper and tin), **brass** (copper and zinc), etc., which may all be dissolved in nitric acid.

There are two classes of copper compounds : the **cuprous** (monovalent ion), derived from **cuprous oxide,** Cu_2O (*e.g.* Cu_2Cl_2), and the **cupric** (divalent ion), derived from **cupric oxide,** CuO (*e.g.* $CuCl_2$). Cuprous salts are insoluble in water, and are white when pure. They are readily converted into cupric salts by oxidation. The dry reactions are the same for both classes of compounds.

Dry Reactions.—1. *Blowpipe Test.*—Copper compounds, when mixed with fusion-mixture and potassium cyanide, and heated on charcoal in the reducing flame, yield metallic copper, which is usually in a more or less flaky condition.

2. *Match Test.*—Metallic copper readily obtained.

3. *Borax Bead.*—In the oxidising flame the bead is green while hot, blue on cooling. In the reducing flame it is red or reddish-brown, often opaque. The red colour is more readily obtained if the bead is moistened with a little stannous chloride before heating.

4. *Flame Test.*—Copper compounds, when strongly heated, colour the flame green. If the platinum wire on which the compound of copper is heated is first dipped in strong hydrochloric acid, the colour imparted to the flame is blue.

Cuprous Compounds.

Reactions in Solution.—Use a solution of **cuprous chloride** in hydrochloric acid, which can be prepared by boiling a small quantity of cupric chloride in strong hydrochloric acid to which is added a few copper turnings.

*1. **Water,** on being added to a solution of cuprous chloride in concentrated hydrochloric acid, produces a heavy white precipitate of **cuprous chloride,** because cuprous chloride is not soluble in dilute hydrochloric acid.

√ *2. **Potassium hydroxide** gives a yellow precipitate of **cuprous hydroxide.**

$$Cu_2Cl_2 + 2KOH = Cu_2(OH)_2 + 2KCl$$

It quickly absorbs oxygen from the air, and becomes converted into black cupric hydroxide. The oxidation is more rapid if the mixture is boiled.

Cupric Compounds.

Use a solution of **copper sulphate.**

***1. Ammonium hydroxide** precipitates from soluble copper salts a bluish-green basic salt, which readily dissolves in an excess, producing a brilliant deep blue solution.

(*a*) $2CuSO_4 + 2NH_4OH = CuSO_4, Cu(OH)_2 + (NH_4)_2SO_4$

(*b*) $CuSO_4, Cu(OH)_2 + 6NH_3 + (NH_4)_2SO_4$

$$= 2([Cu(NH_3)_4]SO_4, H_2O)$$

Addition of alcohol to the blue solution precipitates the copper ammonium compound in the form of a blue crystalline precipitate.

2. Sodium or **potassium hydroxide** produces a voluminous bluish-white precipitate of **cupric hydroxide,** insoluble in excess. On boiling it is converted into black **cupric oxide.**†

(*a*) $CuSO_4 + 2NaOH = Cu(OH)_2 + Na_2SO_4$

(*b*) $Cu(OH)_2 = CuO + H_2O$

***3. Hydrogen sulphide** gives a black precipitate of **cupric sulphide,** soluble in hot nitric acid and in potassium cyanide. It is therefore not precipitated from solutions containing potassium cyanide. See § 7, next page. (*Cf.* Cadmium, § 1, p. 55.)

$$CuSO_4 + H_2S = CuS + H_2SO_4$$

***4. Potassium ferrocyanide** forms a reddish-brown precipitate of **cupric ferrocyanide.** If the solution is very dilute no precipitate is formed, but a reddish-brown coloration is produced. The precipitate is soluble in warm dilute nitric acid.

$$2CuSO_4 + K_4Fe(CN)_6 = Cu_2Fe(CN)_6 + 2K_2SO_4$$

† In presence of many non-volatile organic compounds no precipitation takes place, but a deep blue solution is produced. If the blue solution is warmed with a reducing agent such as dextrose, or treated with phenylhydrazine, in the cold, reduction takes place, and red cuprous oxide is precipitated. (*Cf.* "Fehling's Solution," p. 370.)

***5. Potassium iodide** produces a white precipitate of cuprous iodide.

$$2CuSO_4 + 4KI = Cu_2I_2 + 2K_2SO_4 + I_2$$

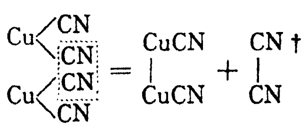
The reaction is only complete in presence of sulphurous acid; for the theoretical explanation of this, see p. 148.

***6.** When a piece of clean iron is placed in a solution of a cupric salt, the iron becomes coated with a covering of red metallic copper.

$$CuSO_4 + Fe = Cu + FeSO_4$$

***7. Potassium cyanide** gives a yellowish-green precipitate of cupr*ic* cyanide, which rapidly loses cyanogen and becomes converted into white cupr*ous* cyanide.

(i) $2CuSO_4 + 4KCN = 2Cu(CN)_2 + 2K_2SO_4$

(ii) 

Excess of potassium cyanide dissolves the cuprous cyanide with formation of potassium cuprocyanide.

$$Cu_2(CN)_2 + 6KCN = 2K_3Cu(CN)_4 \ddagger$$

Potassium cuprocyanide in solution is dissociated into the ions $3K^{\cdot}$ and $Cu(CN)_4'''$. As the complex anion $Cu(CN)_4'''$ is very stable, no precipitate is produced when hydrogen sulphide is passed into the solution or when other reagents for copper are added to it. It is necessary, however, to have the potassium cyanide in considerable excess to completely prevent precipitation with hydrogen sulphide.

8. Drop Reaction.—The solution is made just alkaline with ammonia, and a drop of a 0·1 per cent. solution of sodium

† This may be used as a method for preparing cyanogen. One has only to take a solution of copper sulphate and gradually run a solution of potassium cyanide into the warm solution, by means of a dropping funnel to obtain a constant evolution of cyanogen.

‡ In strong solution the salt is $K_3Cu(CN)_4$, in more dilute solutions $KCu_2(CN)_3$.

diethyl dithio carbamate is added. Copper produces a brown colour (sensitiveness 1 : 10^7). The reaction is selective if iron is removed by filtration after adding the ammonia ; but many other metals in this group produce white precipitates. The reaction is so sensitive that the amount of material taken must be very small.

9. Crystal Test.—A drop of the test solution is evaporated and the residue is dissolved in acetic acid. (*a*) A drop is brought into contact with a drop of mercury thiocyanate reagent (p. 371), when radiating tufts of yellow or green forked crystals of $Cu(CNS)_2Hg(CNS), H_2O$ are produced (*cf.* Fig. 9, p. 139). (*b*) The triple nitrite reaction for potassium (p. 48) may also be used if to one drop is added a little lead acetate followed by an excess of potassium nitrite. The sensitiveness for both reactions is 0·5 γ.

Cadmium.

Dry Reactions.—Metallic cadmium has very much the appearance of zinc, but it is softer and less crystalline in structure. It dissolves in dilute hydrochloric and sulphuric acids with evolution of hydrogen, and is readily soluble in nitric acid. Cadmium salts are colourless or white. The normal soluble salts are acid to litmus paper. The halogen salts of cadmium are only very slightly ionised in solution ; this is especially the case with cadmium iodide. Because of this fact, a solution of cadmium iodide is not readily precipitated by hydrogen sulphide.

1. *Blowpipe Test.*—A brown incrustation of oxide is obtained on charcoal.

2. *Film Test.*—See table, p. 198.

Reactions in Solution.—Use a solution of **cadmium sulphate** or **chloride.**

***1. Hydrogen Sulphide** produces in dilute acid solutions a canary-yellow precipitate of **cadmium sulphide,** insoluble in

ammonium sulphide, in caustic alkalis, and in *potassium cyanide;* but soluble in dilute nitric, hydrochloric, or sulphuric acid. In order to obtain complete precipitation it is necessary that the solution should be only very slightly acid. **In strongly acid solutions no precipitation takes place, because the reaction is reversible.**

$$CdCl_2 + H_2S \rightleftharpoons CdS + 2HCl$$

***2. Potassium cyanide** precipitates white **cadmium cyanide,** soluble in excess.

$$(a) \quad CdCl_2 + 2KCN = Cd(CN)_2 + 2KCl$$
$$(b) \quad Cd(CN)_2 + 2KCN = K_2Cd(CN)_4$$

From this solution cadmium sulphide is precipitated by hydrogen sulphide because the complex anion $Cd(CN)_4''$ is itself slightly ionised into $Cd^{\cdot\cdot}$ and $4CN_4'$. (*Cf.* Copper, p. 54.)

3. Caustic alkalis give a white gelatinous precipitate of **cadmium hydroxide,** insoluble in excess of the precipitant.

$$CdSO_4 + 2KOH = Cd(OH)_2 + K_2SO_4$$

***4. Ammonium hydroxide** produces the same precipitate which *is soluble in excess.* If free acid or if ammonium salts are present no precipitation takes place. (*Cf.* Bismuth, § 2, p. 49.)

5. Drop Reaction.—A drop of a saturated solution of diphenyl carbazide in alcohol is placed on a filter paper, which is allowed to dry and a drop of the test solution, previously made acid with acetic acid (*e.g.* by adding sodium acetate if mineral acid is present) is added. The paper is dried and is held over the ammonia bottle, when violet-blue colour results with 4 γ of cadmium. Chromium gives a similar colour and mercury and magnesium also react, but only in neutral and alkaline solutions, respectively.

6. Crystal Test.—A crystal of oxalic acid is added to the solution when colourless parallelograms are formed (Fig. 10, p. 139). Other metals (especially zinc), which form insoluble oxalates, interfere.

Group Separation.

The metals of the copper and arsenic groups are precipitated together by passing hydrogen sulphide through the dilute acid solution obtained after filtering off the metals of the silver group. The precipitated sulphides are filtered, washed, and digested with hot ammonium sulphide or sodium hydroxide solution ; the latter may, however, only be used when tin salts are not present (see p. 72). This treatment dissolves the sulphides of **arsenic, antimony, tin, platinum,** and **gold,** but leaves the sulphides of **copper, mercury, lead, bismuth,** and **cadmium** unaffected. (A table of separation for the metals of the **copper group** will be found on p. 214.)

Before passing hydrogen sulphide, the solution should be boiled, because the precipitate then comes down in a more granular form, and is more readily filtered and washed. *Great care* must be taken that *sufficient* hydrogen sulphide is used to ensure complete precipitation ; a fresh quantity of gas should be passed through a portion of the filtrate from the sulphides. If a further precipitate is produced, then hydrogen sulphide must be passed through the whole of the filtrate. It is also of extreme importance that the solution is *not* strongly acid, otherwise cadmium will not be precipitated.

CHAPTER V.

THE ARSENIC GROUP.

THE metals of this group are precipitated along with the metals of the copper group as sulphides. They are separated from the sulphides of the copper group by taking advantage of their solubility in alkali sulphides with formation of thio-salts; *e.g.*—

$$As_2S_3 + 3(NH_4)_2S = 2(NH_4)_3AsS_3$$
$$Sb_2S_3 + 3(NH_4)_2S = 2(NH_4)_3SbS_3$$

Arsenic.

Pure arsenic is a brittle and crystalline substance, which has more or less metallic lustre. It becomes dull, however, when exposed to moist air, owing to the formation of a coating of arsenic oxide. It volatilises at a low red heat without melting, producing a characteristic garlic odour. When heated with free access of air, it burns, giving off white fumes of arsenious oxide. On heating with dilute nitric acid arsenic is converted into arsenious acid.

$$2As + 2HNO_3 + 2H_2O = 2H_3AsO_3 + 2NO$$

Strong nitric acid converts it into arsenic acid.

$$6As + 10HNO_3 + 4H_2O = 6H_3AsO_4 + 10NO$$

It is slightly soluble in hydrochloric acid and dilute sulphuric acid. Boiling, strong sulphuric acid converts it into arsenious acid, while with aqua regia arsenic acid is obtained.

The arsenious compounds are derived from arsenious oxide, As_4O_6. With very strong acids, such as hydrochloric acid, this oxide produces the trivalent cation $As^{\cdot\cdot\cdot}$; with bases it

forms the trivalent anion AsO_3'''. The salts containing this anion are called **arsenites.** Arsenious oxide, As_4O_6, in aqueous solution probably forms **arsenious acid,** H_3AsO_3; but it is very feebly ionised, and hence is a very weak acid. The **arsenic** compounds are derived from **arsenic oxide,** As_2O_5. The composition of some of these is such as to suggest the existence of a pentavalent cation, $As^{\cdot\cdot\cdot\cdot\cdot}$; but there is no evidence for the existence of such a cation in solution. All the soluble derivatives of As_2O_5 contain trivalent anions, AsO_4''' or AsS_4''' or derivatives of these. The salts containing AsO_4''' are called **arsenates,** those containing AsS_4''' **thio-arsenates.**

Dry Reactions.

1. Arsen*ites* and arsen*ates*, when heated with a little dry charcoal, are reduced to the metal. This very delicate test

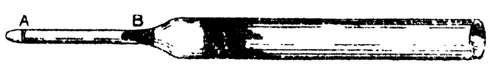


FIG. 11.

may be carried out in a tube drawn out as in Fig. 11, the narrow end A being sealed. A small quantity of the arsenic compound is introduced into the pointed end of the tube at A, and a few fragments of freshly ignited charcoal are inserted at B. First the charcoal is heated to redness, and then the arsenic compound volatilises and passes over the hot charcoal, which must not be allowed to cool. The arsenic compound becomes reduced, and the arsenic condenses in the form of a black mirror, just above the constriction of the tube.

$$As_4O_6 + 6C = 4As + 6CO$$

2. Arsenic compounds, when mixed with charcoal or some other reducing agent, and heated in a tube open at both ends (draught-tube), so that a current of air can pass through, deposit a white crystalline film of As_4O_6 on the cool part of the tube, the arsenic produced at first being oxidised by the air.

3. *Film Test.*—See table, p. 198.

4. All arsenic compounds when heated on charcoal are volatilised, a garlic-like odour being noticed. A white incrustation on the cool portions of the charcoal may also be produced.

***5.** *Gutzeit Test.*—When arsenic compounds are heated in a test-tube with pure **zinc** and **sodium hydroxide,**† **arsenic trihydride** is evolved. If a piece of filter paper which has been moistened with mercuric chloride is held in the mouth of the tube, it is turned yellow. As there is a tendency for the alkaline fluid to spurt out of the tube, the experiment should be carried out as indicated in Fig. 12, the mouth of the test-tube being loosely plugged with a piece of cotton-wool.

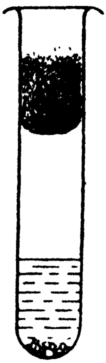


FIG. 12.

A good method is to use magnesium wire or ribbon, and a neutral solution of ammonium sulphate or chloride.

$$Mg + 2NH_4Cl = MgCl_2 + 2NH_3 + H_2$$

The nascent hydrogen given off reduces the arsenic compound to AsH_3, and this, in presence of the ammonia produced at the same time, forms a black or brown stain on the paper moistened with mercuric chloride. The solution to be tested is placed in a test-tube, about 4 grms. of solid ammonium salt and then a piece of magnesium wire added; water is added so that the tube is about one-quarter full. On standing for 15 minutes 0·002 mgrm. gives a reaction.

***6.** *The Berzelius-Marsh Test.*—This test, which is extremely delicate, depends on the formation of arsenic trihydride (arsine, AsH_3) when arsenic compounds are reduced by nascent hydrogen; *e.g.*—

$$As_4O_6 + 24H = 4AsH_3 + 6H_2O$$

In carrying out this test an apparatus for generating hydrogen is fitted up, as shown in Fig. 13. A piece of hard

† Pure sulphuric or hydrochloric acid may also be employed.

glass tube, drawn out as shown in the sketch, is attached to the gas-generating apparatus by means of a piece of rubber tubing. Before applying the test a slow stream of hydrogen, produced from pure zinc and dilute sulphuric acid,† is passed through the apparatus for a few minutes, to expel all the air. As soon as this has taken place, which is shown by the gas burning **quietly** when collected in a test-tube and a light applied, the issuing hydrogen is ignited at A, and a little of the solution to be tested for arsenic is poured down the thistle funnel into the flask. The evolution of hydrogen

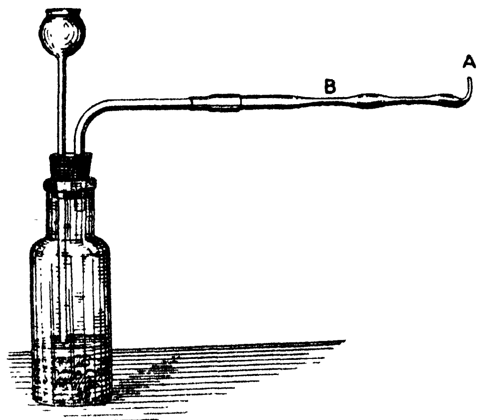


FIG. 13.

becomes much more vigorous, and the flame at A assumes a lilac hue, while at the same time vapours of As_4O_6 are given off.

This method is also used for the quantitative determination of arsenic. A more convenient form of apparatus specially suitable for this purpose is one in which hydrogen is generated by electrolysis inside the apparatus.

† Sulphuric acid does not readily react with pure zinc; but the addition of a few drops of copper sulphate or, better, cadmium chloride solution, will cause a brisk evolution of gas. The hydrogen, however, should not be generated too rapidly, or when the arsenic solution is added the reaction will be very violent. In preparing arsenic trihydride, nitric acid or other oxidising agents should not be present, as they interfere with its formation. Mercury should also be absent.

1. On holding a cold porcelain dish in the flame, a brownish metallic film is deposited upon it.

This deposit of metallic arsenic mixed possibly with a solid hydride of arsenic of uncertain composition, dissolves immediately in **sodium hypochlorite** or in **bleaching powder** solution (distinction from antimony).

$$2As + 5NaOCl + 3H_2O = 2H_3AsO_4 + 5NaCl$$

On touching the deposit or "mirror" with a drop of **ammonium sulphide** on a glass rod, it turns yellow, owing to formation of **sulphide of arsenic.** When there is an excess of ammonium sulphide it dissolves, reappearing again as the ammonium sulphide is carefully evaporated.

2. If the glass tube through which the arsenic trihydride is passing is heated at one of the constrictions, B (Fig. 13), by means of the Bunsen burner, the arsenic trihydride is decomposed, **arsenic** being deposited as a black mirror on the cool part of the tube. On removing the tube from the apparatus, and passing hydrogen sulphide through it, the arsenic mirror being heated at the same time, yellow arsenious sulphide is produced.

3. On passing the gas through a dilute solution of silver nitrate containing a drop or two of free nitric acid, a black precipitate of metallic silver is formed (*cf.* Antimony).

$$AsH_3 + 6AgNO_3 + 3H_2O = 6Ag + H_3AsO_3 + 6HNO_3$$

On neutralising the acid solution, and if necessary adding more silver nitrate, a yellow precipitate of **silver arsenite** is produced.

$$Na_3AsO_3 + 3AgNO_3 = Ag_3AsO_3 + 3NaNO_3$$

Reinsch's Test.—When a piece of freshly cleaned copper foil is placed in a slightly acidified solution of an arsenite and the solution is warmed, the copper becomes coated with a dark grey film of As_2Cu_5. This arsenic compound may be converted into a white sublimate of arsenious oxide by heating the piece of coated copper in a dry test-tube. The copper must have been previously washed with distilled water, and then dried in such

a way as not to remove the coating. This may be effected by pressing the copper between folds of filter paper. **Arsenic** compounds do not show Reinsch's test unless they have first been reduced to the arsenious state, by boiling for some time with strong hydrochloric acid, or, better, with sulphurous acid.

Arsenious Compounds.

Use either a solution of **arsenious oxide** in hydrochoric acid, or of a soluble **arsenite** such as potassium arsenite.

***1. Hydrogen Sulphide** gives, in acid solutions, a yellow precipitate of **arsenic trisulphide.** If the solution is neutral or alkaline, a yellow coloration only is produced. (*Cf.* p. 26.)

$$As_4O_6 + 6H_2S = 2As_2S_3 + 6H_2O$$

$$2K_3AsO_3 + 3H_2S + 6HCl = As_2S_3 + 6H_2O + 6KCl$$

Arsenic trisulphide is insoluble in strong hydrochloric acid (distinction from antimony), but soluble in nitric acid. It is readily soluble in caustic alkali, in calcium hydroxide, ammonium hydroxide, ammonium sulphide, and ammonium carbonate, with formation of thioarsen*ites*.

(1) $$As_2S_3 + 6KOH = K_3AsO_3 + \underset{\text{Potassium thioarsenite}}{K_3AsS_3} + 3H_2O$$

(2) $$As_2S_3 + 3(NH_4)_2S = 2(NH_4)_3AsS_3$$

(3) $$As_2S_3 + 3(NH_4)_2CO_3 = (NH_4)_3AsS_3 + (NH_4)_3AsO_3 + 3CO_2$$

The thioarsenites are decomposed by acids, the sulphide being reprecipitated. As hydrogen sulphide usually escapes when the thio-compounds are decomposed by acids, the reprecipitation is not always quantitative unless more hydrogen sulphide is passed through the mixture.

(*a*) $$K_3AsO_3 + K_3AsS_3 + 6HCl = As_2S_3 + 6KCl + 3H_2O$$

(*b*) $$2(NH_4)_3AsS_3 + 6HCl = As_2S_3 + 6NH_4Cl + 3H_2S$$

***2. Silver nitrate** produces with neutral solutions of arsenites a yellow precipitate of **silver arsenite,** soluble in ammonium hydroxide and in acids.

$$K_3AsO_3 + 3AgNO_3 = Ag_3AsO_3 + 3KNO_3$$

✓ **3. Lead acetate** precipitates white **lead arsenite,** soluble in acetic acid, and also in a large excess of lead acetate, from which it is reprecipitated on boiling. (*Cf.* Lead Arsen*ate*.)

$$2K_3AsO_3 + 3Pb(CH_3COO)_2 = Pb_3(AsO_3)_2 + 6CH_3 . COOK$$

4. A Solution of Iodine in potassium iodide, is decolorised by arsenites. This reaction is used in the volumetric determination of arsenites. It is only quantitative in the absence of free acid, hence sodium bi-carbonate is added to neutralise the free hydriodic acid liberated.

$$H_3AsO_3 + I_2 + 2NaHCO_3 = H_3AsO_4 + 2NaI + 2CO_2 + H_2O$$

Sodium carbonate must not be added because this also decolorises solutions of iodine.

$$3Na_2CO_3 + 6I = NaIO_3 + 5NaI + 3CO_2$$

Arsenic Compounds.

Use either a solution of **arsenic pentoxide** in hydrochloric acid or any soluble **arsenate.**

***1. Hydrogen Sulphide,** when passed into a solution of an arsen*ate*, produces no precipitate immediately, as it is necessary first to reduce the arsen*ate* to an arsen*ite*; during this reduction sulphur is precipitated.

$$2As_2O_5 + 4H_2S = As_4O_6 + 4H_2O + 4S$$

As soon as the reduction has taken place, further addition of hydrogen sulphide precipitates arsenic trisulphide. The reduction and precipitation are facilitated by passing the hydrogen sulphide into a boiling solution, containing an excess of hydrochloric acid.

In order that the sulphide may be at once precipitated, and without deposition of sulphur, the arsen*ate* must first be reduced by adding sulphurous acid until a distinct smell of sulphur dioxide is noticeable, and then boiling until the odour is no longer apparent.

$$2As_2O_5 + 4H_2SO_3 = As_4O_6 + 4H_2SO_4$$

If hydrogen sulphide is now passed, immediate precipitation takes place.

***2. Ammonium sulphide** gives no precipitate with arsenates, but forms **ammonium thioarsenate** $(NH_4)_3AsS_4$. On acidifying with hydrochloric acid and warming, a precipitate of **arsenic pentasulphide** is formed.

$$2(NH_4)_3AsS_4 + 6HCl = As_2S_5 + 6NH_4Cl + 3H_2S$$

***3. Silver nitrate** produces from neutral solutions of arsenates, a reddish-brown precipitate of **silver arsenate,** which is soluble in acids and in ammonium hydroxide.

$$K_3AsO_4 + 3AgNO_3 = Ag_3AsO_4 + 3KNO_3$$

4. Lead acetate throws down, from neutral or acetic acid solutions of arsenates, a white precipitate of **lead arsenate, insoluble** in acetic acid. (*Cf.* Lead Arsen*ite*.)

$$2K_3AsO_4 + 3Pb(CH_3COO)_2 = Pb_3(AsO_4)_2 + 6CH_3 . COOK$$

***5. Magnesia mixture** (see p. 369) produces, from neutral or alkaline solutions of arsen*ates*, a white crystalline precipitate of **magnesium-ammonium-arsenate.**

$$K_3AsO_4 + MgCl_2 + NH_4Cl = (NH_4)MgAsO_4 + 3KCl$$

This reaction is used to separate arsen*ates* from arsen*ites*. (*Cf.* Phosphoric Acid, p. 176.)

Antimony.

Antimony is a white brittle metal. When heated in the air it fuses, and then burns, giving off white fumes of Sb_4O_6. It is almost insoluble in **hydrochloric** and **sulphuric acids,** but will dissolve readily in **hydrochloric acid** to form $SbCl_3$, if nitric acid is added little by little. **Nitric acid** converts it into Sb_2O_5, which is soluble in hydrochloric acid and caustic alkali, forming, *e.g.*, with **potassium hydroxide,** $SbO_2(OK)$. Antimony pentoxide is, however, not readily soluble in caustic alkali after it has been strongly ignited.

Like **arsenic,** antimony forms two series of compounds—antimon*ious* and antimon*ic*. In the **antimonious** compounds,

which are derived from the oxide Sb_4O_6, antimony is trivalent, while it is pentavalent in the **antimonic** compounds, which are derived from the pentoxide Sb_2O_5. Antimony trioxide dissolves in caustic alkalis with formation of a **metantimonite** O : Sb . ONa. Probably in the first case sodium antimonite is produced, but, owing to hydrolysis, this is converted into the metantimonite.

$$(1)\quad Sb_4O_6 + 12NaOH = 4Sb(ONa)_3 + 6H_2O$$

$$(2)\quad Sb(ONa)_3 + H_2O = Sb\begin{cases} {}^{\nearrow}O \\ {}_{\searrow}ONa \end{cases} + 2NaOH$$

Further, antimony tends, like arsenic, to form according to circumstances, either elementary cations or complex anions. In the case of antimonious compounds, the **chloride** $SbCl_3$ ionises slightly into trivalent $Sb^{\cdots}$ cations, while **sodium metantimonite** ionises into monovalent SbO_2' anions.

Solutions of antimony salts where Sb is the cation can only be kept in strongly acid solutions, because, being very slightly dissociated in aqueous solution, they are strongly hydrolysed with formation of insoluble **oxy-salts,** *e.g.* antimony oxychloride.

$$SbCl_3 + H_2O \rightleftharpoons 2HCl + Sb\begin{cases} {}^{\nearrow}O \\ {}_{\searrow}Cl \end{cases}$$

But owing to the property which antimony possesses of substituting the hydroxylic hydrogen of organic compounds, by the monovalent **antimonyl** radical SbO′, *e.g.* the formation of tartar emetic from tartaric acid, antimony can readily be obtained in a condition in which it is soluble in water.

$$4\begin{array}{l} CH.(OH).COOK \\ | \\ CH.(OH).COOH \end{array} + Sb_4O_6 = 4\begin{array}{l} CH(OH).COOK \\ | \\ CH(OH).COO(SbO) \end{array} + 2H_2O$$

Dry Reactions.

1. *Draught Tube.*—When heated in a glass tube open at both ends, white fumes of **antimonious** and **antimonic** oxides are produced, which condense on the cool parts of the tube.

$$2Sb_2S_3 + 9O_2 = Sb_4O_6 + 6SO_2$$

2. *Blowpipe Test.*—When heated on charcoal with fusion mixture and potassium cyanide, compounds of antimony yield a brittle bead of metállic antimony; at the same time, a white incrustation of Sb_4O_6 forms on the charcoal.

3. *Match Test.*—Brittle beads of metallic antimony produced.

4. *Film Test.*—See table, p. 198.

5. *Flame Test.*—Compounds of antimony impart a pale blue coloration to the flame of a Bunsen burner.

Reactions in Solution.

I. Reactions Common to Antimonious and Antimonic Compounds.—1. On placing a piece of zinc in contact with a piece of platinum in a porcelain basin, and then adding a solution of an antimony salt, slightly acidified with hydrochloric acid, the antimony will be deposited on the platinum as a black stain, at the point of contact between the zinc and platinum. The stain dissolves in warm nitric acid.

2. *Berzelius-Marsh Test.*—When antimony compounds are brought in contact with zinc and dilute sulphuric acid in an apparatus for generating hydrogen, as described for arsenic (Fig. 13), **antimony hydride** (stibine, SbH_3) is produced, the issuing jet of gas, on ignition, burning with a bluish-white flame.

(*a*) On holding a cold porcelain dish in the flame, a film of antimony is deposited as a dull brownish-black mirror. This is insoluble in bleaching-powder solution or sodium hypochlorite (distinction from arsenic), but it is soluble in hydrochloric acid, whereas arsenic is almost insoluble.

(*b*) On heating the glass tube, through which the gas is passing, the antimony is deposited on *both* sides of the heated portion (arsenic deposits only on the side furthest from the generating flask). On now detaching the tube, heating and passing hydrogen sulphide through, the mirror is converted into orange antimony sulphide, soluble in concentrated hydrochloric acid (distinction from arsenic).

(*c*) If the gas is passed into a solution of silver nitrate,

acidified with nitric acid, a black precipitate of silver antimonide separates.

$$SbH_3 + 3AgNO_3 = SbAg_3 + 3HNO_3$$

II. Antimonious Compounds.—**Tartar emetic,** or a solution of **antimony trichloride** in hydrochloric acid, may be used for these reactions.

*1. **Hydrogen sulphide** gives a deep orange precipitate with acid solutions of **antimonious sulphide.** If the solution is neutral (*e.g.* tartar emetic), only a red or yellow coloration is produced.

$$2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl$$

It is readily soluble in ammonium sulphide, and in sodium and potassium hydroxides, being converted into **thio**-salts.

(*a*) $Sb_2S_3 + 3(NH_4)_2S = \underset{\text{Ammonium thioantimonite}}{2(NH_4)_3SbS_3}$

(*b*) $Sb_2S_3 + 2KOH = \underset{\text{Potassium thio-metantimonite}}{Sb\begin{cases}S\\SK\end{cases}} + \underset{\text{Potassium oxythio-metantimonite}}{Sb\begin{cases}S\\OK\end{cases}} + H_2O$

From these solutions the trisulphide is reprecipitated by addition of hydrochloric acid.

(*a*) $2(NH_4)_3SbS_3 + 6HCl = Sb_2S_3 + 6(NH_4)Cl + 3H_2S$

(*b*) $KS.SbS + KS.SbO + 2HCl = Sb_2S_3 + 2KCl + H_2O$ †

Antimony sulphide is insoluble in ammonium carbonate (distinction from arsenic), but readily soluble in warm, concentrated hydrochloric acid (distinction from arsenic).

$$Sb_2S_3 + 6HCl \rightleftharpoons 2SbCl_3 + 3H_2S$$

*2. **Sodium** or **potassium hydroxide** gives a white precipitate of **antimony trioxide,** soluble in excess to form sodium or potassium antimon*ite*.

(*a*) $2SbCl_3 + 6KOH = Sb_2O_3 + 6KCl + 3H_2O$

(*b*) $Sb_2O_3 + 2KOH = \underset{\text{Potassium metantimonite}}{2KSbO_2} + H_2O$

† Precipitation of antimony sulphide is not usually quite complete, unless more hydrogen sulphide is passed through the solution.

***3. Water** produces with antimony trichloride a white precipitate of **antimonious oxychloride**, due to hydrolysis of the feebly ionised trichloride.

$$SbCl_3 + H_2O \rightleftharpoons SbOCl + 2HCl$$

This is soluble in tartaric acid and tartrates. (*Cf.* Bismuth, p. 49, § 3.)

***4. Silver nitrate**, when added to an alkaline solution of an antimoni*ous* salt, free from chlorides, produces a black precipitate of **silver monoxide** and **metallic silver.** Only a part of this is soluble in ammonia, *viz.* the silver monoxide (*cf.* Antimonic Compounds, § 2). It must be borne in mind that, in producing an alkaline solution of an antimoni*ous* salt, a precipitate of the oxide is first produced (*cf.* Reaction, 2, p. 68), which then dissolves in excess of the hydroxide, producing sodium or potassium antimon*ite.*

5. Drop Reaction.—Acidic solutions of antimony give a fine white crystalline precipitate with pyrogallol. Precipitates from other metals are soluble in acid.

III. Antimonic Compounds.—Use **potassium antimonate.**

***1. Hydrogen sulphide** produces an orange precipitate of **antimony pentasulphide,** mixed with antimony trisulphide and sulphur. The principal reaction may be expressed as follows :—

$$2K_3SbO_4 + 5H_2S + 6HCl = Sb_2S_5 + 6KCl + 8H_2O$$

The precipitate is soluble in alkali sulphides and in sodium and potassium hydroxide, thioantimon*ates* being formed.

(*a*) $Sb_2S_5 + 3(NH_4)_2S = \underset{\text{Ammonium thioantimonate}}{2(NH_4)_3SbS_4}$

(*b*) $Sb_2S_5 + 6NaOH = \underset{\text{Sodium thio-antimonate}}{Na_3SbS_4} + \underset{\text{Sodium thio-oxy-antimonate}}{(NaO)_3SbS} + 3H_2O$ †

Antimony pentasulphide is insoluble in ammonium carbonate (distinction from arsenic).

2. Silver nitrate, when added to a solution of an alkali

† See footnote, p. 68.

salt (*e.g.* potassium antimon*ate*), produces a white precipitate of **silver antimonate.**

$$K_3SbO_4 + 3AgNO_3 = Ag_3SbO_4 + 3KNO_3$$

The precipitate is readily soluble in ammonium hydroxide. This reaction serves to distinguish between an antimon*ious* and an antimon*ic* salt. (*Cf.* § 4, p. 69.)

*3. On warming an antimon*ate* with **hydrochloric acid,** which must be added in sufficient quantity to dissolve the oxychloride first produced, and adding **potassium iodide,** the solution becomes a deep brown, owing to liberation of free iodine. This reaction is not given by antimon*ious* compounds, but, since they often contain traces of antimon*ic* compounds, a slight brown coloration may be produced.

4. **Crystal Test.**—A crystal of pyrogallol is added to a drop of a slightly acid solution of antimony when small characteristic crystals appear. Other metals do not interfere as the precipitates they produce are soluble in acid.

Tin.

Tin is soluble in boiling concentrated hydrochloric acid, with the formation of stann*ous* chloride. It is converted by concentrated nitric acid into a white powder of **metastannic acid.**

$$3Sn + 4HNO_3 + H_2O + 3SnO(OH)_2 + 4NO$$

This is insoluble in concentrated hydrochloric acid, but is converted by it into metastann*ic* chloride, which dissolves in water; if, therefore, the excess of hydrochloric acid is poured off, and water is added, the precipitate dissolves. Dilute nitric acid converts tin into **stannous nitrate** with evolution of hydrogen.

$$Sn + 2HNO_3 = Sn(NO_3)_2 + H_2$$

Part of the nitric acid is reduced by the nascent hydrogen, with the formation of ammonia.

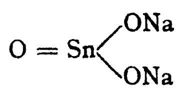
$$4Sn + 10HNO_3 = 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

Tin dissolves readily in aqua regia, being converted into stann*ic* chloride.

$$Sn + 2NOCl + Cl_2 = SnCl_4 + 2NO\dagger$$

It forms many alloys, the analysis of which is effected by dissolution in nitric acid. Tin also resembles arsenic, but in the case of tin the tendency to form elementary cations is more marked than with either arsenic or antimony. Tetravalent tin, however, has still a very much greater tendency to form anions than to function as an elementary cation. Indeed, stannic chloride in aqueous solution hydrolyses into unionised $Sn(OH)_4$ and hydrochloric acid.

Tin forms two classes of compounds, the **stannous** derived from **stannous oxide** SnO, and the **stannic,** derived from **stannic oxide** SnO_2. The **stannous** compounds form the stann*ites*, *e.g.* potassium stann*ite*, $Sn(OK)_2$. The stann*ic* compounds form the **stannates,** *e.g.* **sodium stannate,**



Dry Reactions.

1. *Blowpipe Test.*—When heated on charcoal with fusion mixture and potassium cyanide, compounds of tin are reduced, malleable metallic beads being obtained, which do not mark paper, and thus are easily distinguished from lead. Part of the metal is at the same time oxidised to **stannic oxide,** which forms a white incrustation on the charcoal.
2. *Match Test.*—Small beads of metallic tin are obtained.
3. *Flame Test.*—A bluish-green coloration is produced.
4. *Film Test.*—See table, p. 198.

† See "aqua regia," p. 364.

Reactions in Solution.

Stannous Compounds.

I. Use a solution of **stannous chloride.**

*1. **Hydrogen sulphide** produces a chocolate-brown precipitate of **stannous sulphide.**

$$SnCl_2 + H_2S = SnS + 2HCl$$

This is soluble in warm concentrated hydrochloric acid, in oxalic and tartaric acids, and in yellow ammonium sulphide. (It is almost insoluble in colourless ammonium sulphide.) Generally speaking, it is insoluble in potassium or sodium hydroxide, but occasionally it becomes oxidised and then dissolves quite readily. Therefore when tin is present, it is not wise to use NaOH in separating the copper and arsenic groups.

$$(NH_4)_2S_2 + SnS = \underset{\text{Ammonium thiostannate}}{(NH_4)_2SnS_3}$$

From its solution in ammonium sulphide it is reprecipitated by dilute hydrochloric acid as **stannic sulphide.**

$$(NH_4)_2SnS_3 + 2HCl = SnS_2 + 2(NH_4)Cl + H_2S$$

2. **Potassium** or **sodium hydroxide** gives a white precipitate of **stannous hydroxide.**

$$SnCl_2 + 2KOH = Sn(OH)_2 + 2KCl$$

This is soluble in excess of the reagent, forming an alkali stann*ite*.

$$Sn(OH)_2 + 2KOH = \underset{\text{Potassium stannite}}{K_2SnO_2} + 2H_2O$$

*3. **Mercuric chloride** produces a white precipitate of **mercurous chloride.** *If the stannous salt is in excess the precipitate rapidly turns grey,* owing to further reduction to metallic mercury. (*Cf.* Mercury, p. 41, § 3.)

$$(a) \quad SnCl_2 + 2HgCl_2 = Hg_2Cl_2 + SnCl_4$$
$$(b) \quad SnCl_2 + Hg_2Cl_2 = 2Hg + SnCl_4$$

4. On placing a piece of zinc in a *slightly* acid solution of either a stann*ous* or a stann*ic* salt, the tin is deposited on the zinc as a soft crystalline mass. The test is best made by holding a piece of platinum wire in contact with the zinc in the solution. A stain also appears on the platinum, but this dissolves when the zinc is removed (distinction from antimony).

***5. Hydrogen aurichloride** in acid solutions is reduced by stann*ous* salts to metallic gold.

$$3SnCl_2 + 2HAuCl_4 = 3SnCl_4 + 2Au + 2HCl$$

In neutral solutions the precipitate is purple; in very dilute solutions only a purple coloration is produced—"*purple of Cassius.*" The reaction is more delicate in the presence of a small quantity of stann*ic* chloride, and may be used as a **Drop Reaction** (sensitiveness 0·1 γ).

6. Potassium permanganate in acid solution, or other oxidising agents, oxidise stann*ous* salts to stann*ic* salts. The permanganate is decolorised and this reaction can be employed for the determination of tin.

$$5SnCl_2+2KMnO_4+16HCl=5SnCl_4+2MnCl_2+2KCl+8H_2O$$

***7.** If **ferric chloride** is added to **potassium ferricyanide** the solution darkens without the formation of a precipitate (p. 94). The addition of a little stannous chloride produces an immediate blue precipitate of **ferrous ferricyanide** (Turnbull's Blue), the ferric chloride having been reduced to ferr*ous* chloride (p. 94, § 3).

(*a*) $$SnCl_2 + 2FeCl_3 = SnCl_4 + 2FeCl_2$$

(*b*) $$3FeCl_2 + 2K_3Fe(CN)_6 = Fe_3[Fe(CN)_6]_2 + 6KCl$$

8. Drop Reaction.—A drop of the solution is placed on a filter paper which has previously been treated with a saturated solution of cacotheline in water. A violet spot is produced (sensitiveness 2 γ) in the presence of all other common metals except titanium, the chloride of which is the only one sufficiently powerful to effect this reduction.

9. Crystal Test.—A crystal of potassium oxalate produces H-shaped crystals of stannous oxalate (sensitiveness 0·15 γ).

Stannic Compounds.

II. Use a solution of **stannic chloride** in hydrochloric acid, or in water.

***1. Hydrogen sulphide** gives a yellow to yellowish-brown precipitate of **stannic sulphide.**

$$SnCl_4 + 2H_2S = SnS_2 + 4HCl$$

This is soluble in hot hydrochloric acid, in sodium and potassium hydroxides, in colourless or yellow ammonium sulphide, and in alkali sulphides.

$$2SnS_2 + 4NaOH = \underset{\text{Sodium oxythiostannate}}{SnS(ONa)_2} + \underset{\text{Sodium thiostannate}}{Na_2SnS_3} + 2H_2O$$

$$SnS_2 + (NH_4)_2S = \underset{\text{Ammonium thiostannate}}{(NH_4)_2SnS_3}$$

2. Sodium or potassium hydroxide produces a white precipitate of stannic hydroxide—

$$SnCl_4 + 4NaOH = Sn(OH)_4 + 4NaCl$$

which is soluble in excess of the precipitant and in acids. When dried over sulphuric acid it is converted into $SnO(OH)_2$ which is almost insoluble in dilute acids. On ignition, it is converted into SnO_2, which is quite insoluble in acids.

3. Ammonium hydroxide behaves in the same manner. If tartaric acid is present, only metastannic acid is precipitated.

4. Sodium sulphate** or **ammonium nitrate,** when added to hot neutral solutions of stann*ates* precipitates **stann*ic or **metastann*ic* acid.**

$$SnCl_4 + 4Na_2SO_4 + 2H_2O = SnO_2 + 4NaCl + 4NaHSO_4$$

Stann*ic* sulphate is first formed, and is then hydrolysed by the action of the water.

*5. Stannic salts are reduced to stannous salts when boiled with hydrochloric acid and copper turnings or zinc, and will then give the tests for stannous compounds.

6. **Drop Reaction.**—The reaction described for stannous compounds (§ 8) may be applied if the salt is first reduced to the stannous state.

Gold.

Gold is not oxidised when heated in the air. It is insoluble in acids, but is soluble in aqua regia, being converted into hydrogen aurichloride.

$$2Au + 2HNO_3 + 8HCl = 2HAuCl_4 + 4H_2O + 2NO$$

It also dissolves in bromine water and in potassium cyanide solution in the presence of oxidising agents, such as hydrogen peroxide. On ignition all gold compounds are decomposed into the metal.

Dry Reactions.—1. *Blowpipe Test.*—Heated on charcoal with fusion mixture and borax, a yellow malleable bead of metallic gold is obtained.

2. *Match Test.*—The charred end becomes covered with a thin coating of metallic gold.

Reactions in Solution.—Use a solution of **gold chloride** (hydrogen aurichloride).

*1. **Hydrogen sulphide** gives in cold solutions a black precipitate of **auric sulphide.**

$$2HAuCl_4 + 3H_2S = Au_2S_3 + 8HCl$$

If the solution is boiling, a reddish-brown precipitate of **aur*ous* sulphide** mixed with metallic gold is obtained, which on continued boiling is entirely converted into metallic gold.

$$8HAuCl_4 + 3H_2S + 12H_2O = 8Au + 3H_2SO_4 + 32HCl$$

Both aurous and auric sulphides are insoluble in ordinary acids, but are soluble in aqua regia; and also in ammonium

sulphide and in sodium sulphide. From the last they are reprecipitated on addition of acids, the colour of the reprecipitated sulphide varying from yellow to dark brown.

*2. **Ammonium hydroxide** produces a yellowish-orange precipitate of **fulminate of gold** ($AuNH.NH_2$). On drying and heating this substance it explodes violently.

*3. **Potassium** or **sodium hydroxide** produces a brown precipitate of auric hydroxide from strong solutions, which is soluble in excess with formation of aurate ; in weak solutions no precipitate is formed.

$$(a) \quad HAuCl_4 + 4KOH = Au(OH)_3 + 4KCl + H_2O$$

$$(b) \quad Au(OH)_3 + KOH = Au\begin{cases} =O \\ -OK \end{cases} + 2H_2O$$

*4. Reducing substances, such as **oxalic acid,** precipitate metallic gold on warming, as a brownish powder, which on rubbing becomes burnished, and shows the yellow colour of gold. The gold sometimes forms a mirror on the sides of the tube.

$$2HAuCl_4 + 3\begin{matrix} COOH \\ | \\ COOH \end{matrix} = 2Au + 8HCl + 6CO_2$$

Ferrous sulphate also reduces solutions of gold in the cold.

$$HAuCl_4 + 3FeSO_4 = Au + Fe_2(SO_4)_3 + FeCl_3 + HCl$$

*5. **Stannous chloride** gives (especially in presence of a little stann*ic* chloride) a brownish to purple-coloured precipitate (see Stannous Reactions, § 5, p. 73).

*6. An alkaline solution of **hydrogen peroxide** produces a precipitate of metallic gold—

$$2HAuCl_4 + 3H_2O_2 + 8NaOH = 2Au + 8NaCl + 8H_2O + 3O_2$$

The colour of the solution varies from brownish-black to greenish-purple ; the reaction is very delicate.

7. **Crystal Test.**—A particle of hexamethylene tetramine is added to the solution, when pale yellow needles or thin plates are produced in the absence of mercury or silver.

Platinum.

Platinum does not oxidise when heated in the air, and it is insoluble in all single acids, but is soluble in aqua regia. On ignition of its salts, metallic platinum is obtained. It is found in association with the "platinum metals" the chief of which are palladium, osmium, and iridium.

Dry Reactions.—1. *Blowpipe Test.*—When ignited on charcoal with fusion mixture and potassium cyanide, compounds of platinum are reduced to a dark-grey powder of the **metal,** which is insoluble in ordinary acids, but soluble in aqua regia.

2. *Match Test.*—A dark-grey powder of **metallic platinum** is produced.

Reactions in Solution.

Use a solution of **platinum chloride** † (hydrogen platinichloride).

*1. **Hydrogen sulphide** produces from cold solutions a dark chocolate-coloured precipitate of **platinum sulphide.** The precipitation takes place only after some time.

$$H_2PtCl_6 + 2H_2S = PtS_2 + 6HCl$$

It is insoluble in single acids, but dissolves in aqua regia. It is also soluble in ammonium sulphide.

*2. **Potassium** or **ammonium hydroxide,** in the presence of hydrochloric acid, gives a yellow crystalline precipitate of **potassium or ammonium platinichloride.** The precipitation is more complete if an equal bulk of absolute alcohol be added.

$$H_2PtCl_6 + 2NH_4Cl = (NH_4)_2PtCl_6 + 2HCl$$

It is best to carry out this test as a **drop-reaction** on a watch-glass, two or three drops of hydrogen platinichloride being

† Platinic chloride is really hydrogen platinichloride, and should be written H_2PtCl_6. In solution it is ionised into the ions $2H^{\cdot}$ and $PtCl_6''$; it is therefore incorrect to write it as $PtCl_4$, the ions of which would be $Pt^{\cdot\cdot\cdot\cdot}$ and $4Cl'$.

added to a drop or two of ammonium or potassium chloride to which has been added one drop of hydrochloric acid, and finally an excess of alcohol. The platinichloride then separates out in form of golden spangles.

3. Stannous chloride gives no precipitate, but the **colour** changes from yellow to brownish-red, the platinic salt being reduced to a platinous salt.

$$H_2PtCl_6 + SnCl_2 = H_2PtCl_4 + SnCl_4$$

4. Metallic zinc or iron precipitates finely-divided platinum.

$$H_2PtCl_6 + 2Zn = Pt + 2ZnCl_2 + 2HCl$$

***5. Formaldehyde** produces a precipitate of black metallic platinum from boiling alkaline solutions.

$$H_2PtCl_6 + HCHO + 6KOH = Pt + CO_2 + 6KCl + 5H_2O$$

6. Crystal Test.—Potassium chloride gives well-defined yellow octahedra of K_2PtCl_6 with solutions of platinic chloride. Dilute solutions should first be concentrated.

7. Distinction from other Platinum Metals.—(*a*) A 0·2 per cent. solution of rubianic acid in acetic acid gives a precipitate with platinum; a blue colour in warm and neutral solution with ruthenium; and a red colour or precipitate soluble in dilute hydrochloric acid with palladium. (*b*) A saturated solution of α-nitroso-β-naphthol in 50 per cent. acetic acid gives a brown precipitate of Pd $(C_{10}H_6NO_2)_2$, with palladium, but not with platinum. (*c*) Addition of sodium hydroxide followed by warming, acidification with hydrochloric acid, and addition of alcohol and potassium iodide produces a precipitate with platinum, but not with iridium owing to the solubility of $K_3(IrCl_6)$.

Molybdenum.

This metal is one of the rarer elements, being only found in comparatively small quantities. The most important oxide MoO_3 is acidic, but it also forms MoO, Mo_2O_3, and MoO_2 which are basic.

Dry Reactions.—1. *Borax Bead*, yellow while hot, in reducing flame dark brown, may become opaque with large quantities of molybdenum.

2. *Blowpipe Test.*—When heated on charcoal a grey powder of the metal is produced, which is surrounded by a blue and white incrustation of oxides.

3. *Film Test.*—Metal film : black with blue edges, soluble in 20 per cent. HNO_3 and in NaOCl.

4. *Oxide Film.*—Colourless (may be slightly blue). **HI** : blue which increases in depth when breathed on. **Sulphide** : add one or two drops of $(NH_4)_2S$ and gently evaporate off, brown film becomes colourless on moistening with NaOCl.

Reactions in Solution.—Use a solution of ammonium molybdate $(NH_4)_6Mo_7O_{24}$, $4H_2O$.

1. **Dilute mineral acids** precipitate from solutions, which are not too dilute, white molybdic acid, soluble in excess of the acid, distinction from tungstic acid which is insoluble.

$$(NH_4)_6Mo_7O_{24} + 6HCl + 4H_2O = 7H_2MoO_4 + 6NH_4Cl$$

2. **Concentrated sulphuric acid.**—When a trace of a molybdenum salt is moistened with concentrated sulphuric acid in a porcelain basin and heated until fumes of sulphuric acid are given off, and is then, after cooling, moistened with alcohol, an intense blue coloration is produced. The coloration is due to the formation of the sesquioxide, Mo_2O_3.

3. **Hydrogen sulphide** first reduces the molybdic oxide to the dioxide which causes the solution to become blue. As, however, an excess is added, a brown precipitate of the sulphide is gradually formed. The molybdenum sulphide, MoS_3, is soluble in alkali sulphides, and is reprecipitated again on addition of acids.

$$MoS_3 + (NH_4)_2S = (NH_4)_2MoS_4$$

It is rather a difficult matter to precipitate molybdenum completely as sulphide. This can only be done by boiling the solution after it has become brown, saturating again with gas, allowing to stand a short time, and again boiling. This

usually requires repeating several times. The end of the operation can be seen by the supernatant liquor becoming colourless.

4. **Mercurous nitrate** gives, from neutral solutions, a yellow precipitate of mercurous molybdate, which is soluble in nitric acid. (*Cf.* Tungsten.)

5. **Sodium phosphate,** when added to a molybdate strongly acidified with nitric acid, gives, on warming, a yellow crystalline precipitate of ammonium phosphomolybdate. (*Cf.* Phosphoric Acid, p. 119.)

6. **Ammonium thiocyanate** produces no coloration in acidified solutions of a molybdate, but, on adding a small piece of zinc, or a few drops of a solution of stannous chloride, an intense blood-red coloration of molybdenum thiocyanate is produced. Phosphoric acid does not discharge the colour, **distinction from iron.** On shaking the coloured solution up with ether, the thiocyanate dissolves in it, forming an orange red solution which becomes carmine red owing to the oxidising action of the air.

Detection of Molybdenum in Presence of other Metals.—In a systematic examination of the metals, molybdenum would be found in the arsenic group owing to its forming a thiomolybdenate with ammonium sulphide. It can be distinguished from As, Sb, Sn, Se, Te, and Ge, all of which occur in this group, by heating a small quantity of the dry precipitate with concentrated sulphuric acid (§ 2, p. 79). Or by warming a small quantity of the precipitate with nitric acid, and then adding ammonium thiocyanate to the diluted solution and heating as in § 6, above.

Selenium.

This element is widely distributed in nature. It is often obtained in sulphur-bearing minerals. When such sulphides are used for the manufacture of sulphuric acid by the chamber process, the selenium becomes deposited as a mud at the

bottom of the chambers. It is not unusual therefore to find chamber acid contaminated with selenium.

Selenium forms two acids, selenious H_2SeO_3 and selenic H_2SeO_4, corresponding to sulphurous and sulphuric acids (see also Tellurium).

Reactions in Solution.—Use a solution of potassium selenite, K_2SeO_3.

1. Hydrogen sulphide in acid solutions produces a reddish-yellow sulphide, which contains sulphur and is soluble in ammonium sulphide.

$$H_2SeO_3 + 2H_2S = 3H_2O + Se + 2S$$

2. Reducing agents all precipitate metallic selenium, usually as a red precipitate. Stannous chloride, ferrous sulphate, zinc or hydriodic acid (KI + HCl) act in cold acid solutions and the last is used to distinguish selenium from tellurium. Sulphur dioxide or hydroxylamine or hydrazine hydrochlorides require prolonged boiling.

3. Copper sulphate gives a green-blue precipitate with selenites but not with selenates.

Drop Reaction for Selenium in Sulphuric Acid.—To the sulphuric acid add a few crystals of codeine, when a green coloration shows the presence of selenium.

Tellurium.

This element occurs less frequently than selenium, with which it is closely related. It is blue-white and brittle and burns with a blue flame, forming the dioxide, TeO_2. It forms tellurous and telluric acids analogous to those of sulphur and selenium, *viz.* H_2TeO_3 and H_2TeO_4.

Reactions in Solution.—Use potassium tellurate or tellurite.

1. Hydrogen sulphide precipitates brown TeS_2 from acid solutions of tellurates or tellurites. No precipitate is formed in the former case in the cold, and this may be used to separate tellurium from the heavy metals. The sulphide decomposes

into tellurium and sulphur, and is soluble in ammonium sulphide.

2. Reducing agents.—Sulphur dioxide, phosphoric acid, hydroxylamine hydrochloride, hydrazine or zinc precipitates metallic tellurium. Hot concentrated solutions are usually required.

$$N_2H_4, 2HCl + K_2TeO_3 = 3H_2O + N_2 + Te + 2KCl$$

Hydriodic acid or ferrous sulphate produces no reduction (distinction from selenium).

3. Drop Reaction.—A solution of tellurium in concentrated sulphuric acid is deep red (distinction from selenium), but becomes black on dilution owing to deposition of tellurium.

$$TeSO_3 + H_2O = Te + H_2SO_4.$$

Summary.

Arsenic, antimony, and tin are on the border-line between metals and non-metals. They all possess the distinctive feature of metals, *viz.* the capacity of forming at least one elementary cation. Arsenic and antimony just satisfy that condition and no more, since the trichlorides of arsenic and antimony are ionised in acid solutions, though to a very small extent; in aqueous solutions they are almost completely hydrolysed. The existence of at least the tendency to form elementary cations is shown by the precipitation of the sulphides of these metals by hydrogen sulphide. On the other hand, these three elements have a much more marked tendency to form complex anions—a characteristic, though not an exclusive characteristic, of the **non-metals**: indeed, all of their oxides dissolve readily in caustic alkalis (many of them even in ammonia), owing to the formation of soluble salts whose anions contain the original element. Similarly their sulphides dissolve in alkali hydroxides and sulphides, forming soluble **thio-salts**, whose anions contain these elements; in the **thio-salts** sulphur takes the place occupied by oxygen in the anion of the normal oxygen salt.

The analytical separation of the arsenic group from the copper group is founded on the formation of these soluble thio-salts, and as the sulphides of **gold** and **platinum** likewise dissolve in caustic alkalis and ammonium sulphide, they are, for analytical purposes, also included in this group. As the acids which contain these anions are but feebly ionised, extensive hydrolysis of the salts takes place in aqueous solution ; hence the **alkaline** reaction of the **arsenites** and **arsenates.**

The **sulphides** of these three elements, especially those of arsenic and tin, have a great tendency to form "colloidal" solutions ; hence arsenious sulphide is not readily precipitated from a neutral solution, but the presence of excess of hot **hydrochloric acid** accelerates its precipitation : on the other hand, **stannic sulphide** is not precipitated in strongly acid solutions ; hence complete precipitation of both sulphides requires intelligent manipulation. Owing to the tendency of stannic sulphide to assume the hydrosol condition, the filtration of this sulphide is often tedious. The addition of sodium sulphate or other electrolyte to the solution promotes coagulation of the precipitate, and so facilitates filtration, and prolonged standing in contact with hydrogen sulphide has the same effect, especially in the warm.

Sulphide of arsenic is insoluble in **hydrochloric acid,** while the sulphides of **antimony** and **tin** readily dissolve in the concentrated acid when warmed. **Stannic** and **stannous sulphides** are not precipitated in presence of **oxalic acid,** while antimony sulphide is precipitated under these conditions. This property may be employed in the separation of these elements.

Separation of Arsenic, Antimony, and Tin.—The separation of the metals of the **arsenic group** is one which requires considerable care. The precipitate obtained by passing hydrogen sulphide through the solution from the **silver group,** is filtered and washed with hot water. It is then removed from the filter paper, and boiled for several minutes with **yellow ammonium sulphide (stannous sulphide** is insoluble in colourless

ammonium sulphide); a little water is then added, and the liquid is again filtered. The filtrate contains the metals of the arsenic group as **thio-salts.** The residue consists of the metals of the copper group as **sulphides.**

The **solution** containing the **thio-salts** is acidified with dilute hydrochloric acid. This precipitates **arsenic, antimony,** and **tin** as sulphides, together with a considerable quantity of sulphur from the yellow ammonium sulphide. The precipitate is filtered off and boiled with concentrated hydrochloric acid till no more hydrogen sulphide is given off. The sulphides of antimony and tin dissolve, but arsenious sulphide is unacted upon. After the arsenious sulphide has been filtered off, the antimony and tin are separated by taking advantage of the insolubility of antimony sulphide and the solubility of tin sulphide in a solution of oxalic acid.

In order to carry out this separation the strongly acid solution is made just alkaline with ammonia (an excess should on no account be used), then about 4 grms. of solid oxalic acid are added, and the solution is boiled.† Hydrogen sulphide is now rapidly passed through the hot solution until no further precipitate is produced.

The **precipitate,** which consists of antimony sulphide, is filtered off and well washed first with dilute oxalic acid, and then with hot water.

The **solution** is made slightly alkaline with ammonium hydroxide (a slight precipitate will be produced), and then ammonium sulphide added until a perfectly clear solution is obtained. On now adding a slight excess of **acetic acid** ‡ the tin is precipitated as sulphide, and some sulphur will be precipitated along with it. Instead of adding ammonium sulphide, the solution after the addition of ammonia may be made

† When the amount of tin exceeds 0·5 grm., correspondingly larger quantities of oxalic acid must be employed.

‡ Highly ionised acids, such as hydrochloric acid, must not be employed, because they would liberate the oxalic acid, and thus prevent the precipitation of the tin as sulphide.

slightly acid with acetic acid, and hydrogen sulphide passed through it.

The presence of **antimony** may be confirmed by the film reaction, the sulphide being taken up upon an asbestos thread and moistened with strong hydrochloric acid.

The **tin** may be confirmed by dissolving the sulphide in a little moderately-strong, hot hydrochloric acid, and adding a small crystal of potassium chlorate. If there is much sulphur left, filter. Now add a piece of zinc to the clear solution, and boil until both the zinc and any precipitated tin have dissolved: it may be necessary to add a little more strong hydrochloric acid. Filter from any undissolved substance, add two or three drops of a solution of ferric chloride, and then a few drops of a freshly prepared solution of potassium ferricyanide: a blue precipitate or coloration **confirms tin.** (See § 7, p. 73.)

Arsenic can best be confirmed by dissolving the precipitate in a little nitric acid, and then neutralising with ammonia. A few drops of the solution are then tested by the modified Gutzeit test (§ 5, p. 60). As, however, this test is extremely delicate, and as it is very difficult to obtain reagents quite free from arsenic, it is best to first do a blank experiment with the reagents to be employed, and then a second experiment with the solution under examination. If in the second experiment there is a very distinct coloration, whereas there was none or only a slight coloration in the blank, then the presence of arsenic is confirmed.

When considerable quantities of arsenic are present it may be confirmed by converting it into magnesium ammonium arsenate $Mg(NH_4)AsO_4$. In order to do this, dissolve the precipitate in a few c.c. of fuming nitric acid and boil until no more fumes are given off. Evaporate to about one-third its bulk, dilute with a little water, add an excess of strong ammonia, and then a few c.c. of a solution of magnesium chloride. Stir well with a glass rod, and a white crystalline precipitate shows the presence of arsenic. When only very

small quantities of arsenic are present the precipitate will take some time to form, but if no precipitate is produced within 10 hours then arsenic is not present.

Gold and Platinum.—In a mixture of gold and platinum chlorides, the gold can be separated by shaking up the mixed solution with ether. Gold chloride is soluble, platinum chloride is not. The micro-reactions given are excellent confirmatory texts.

CHAPTER VI.

THE IRON GROUP.

Aluminium.

ALUMINIUM is very similar in its analytical reactions to beryllium (p. 109). It is readily soluble in hydrochloric acid, with evolution of hydrogen. Cold dilute sulphuric acid has very little action on it, and even on boiling the action is very slow. Nitric acid, also, has very little action, owing probably to the formation of a thin protective film of oxide. It dissolves readily in sodium and in potassium hydroxide, with the formation of an **aluminate.**

$$2Al + 6KOH = 2Al(OK)_3 + 3H_2$$

Dry Reactions.—On ignition, compounds of aluminium are converted into the oxide, which becomes incandescent when strongly heated. On adding to the alumina so produced a drop of a solution of cobalt nitrate, and again igniting, a brilliant blue coloration is produced. This test can be carried out by heating on charcoal; or a piece of filter paper may be moistened with a solution of an aluminium salt and a drop of cobalt nitrate. If the paper is dried over the Bunsen flame and then ignited, the ash is coloured blue (p. 11). The test is not conclusive in presence of other oxides or of phosphates or borates, which produce similar effects.

Reactions in Solution.—Use a solution of **potash alum,** which ionises into $K^{\cdot}$, $Al^{\cdot\cdot\cdot}$, and SO_4'' ions.

*1. **Ammonium hydroxide** gives a white gelatinous precipitate of **aluminium hydroxide,** slightly soluble in excess,

but insoluble in presence of ammonium chloride, or on boiling.

$$Al_2(SO_4)_3 + 6NH_4OH = 2Al(OH)_3 + 3(NH_4)_2SO_4$$

*2. **Potassium** or **sodium hydroxide** produces the same precipitate, readily soluble in excess forming an **aluminate.** No precipitation of the hydroxide occurs on boiling.

$$Al(OH)_3 + 3NaOH = Na_3AlO_3 + 3H_2O$$

The aluminium hydroxide is reprecipitated from this solution by addition of excess of ammonium chloride, the precipitation from strong solutions being only partial in the cold, although it is completed by boiling, even with dilute solutions.

$$Na_3AlO_3 + 3NH_4Cl = Al(OH)_3 + 3NaCl + 3NH_3$$

The cause of this precipitation is the formation of ammonium aluminate $(NH_4)_3AlO_3$, which is then completely hydrolysed.

Aluminium hydroxide is not precipitated in the presence of non-volatile organic acids such as tartaric or citric acid; excess of sugar or glycerol likewise prevents precipitation.

3. **Ammonium sulphide** also precipitates **aluminium hydroxide,** the precipitation being complete in presence of ammonium chloride. Aluminium sulphide is probably first produced, but is hydrolysed to form the hydroxide.

(*a*) $Al_2(SO_4)_3 + 3(NH_4)_2S = Al_2S_3 + 3(NH_4)_2SO_4$

(*b*) $Al_2S_3 + 6HOH = 2Al(OH)_3 + 3H_2S$

4. **Sodium phosphate** gives a white precipitate of **aluminium phosphate.**

$$Al_2(SO_4)_3 + 2Na_2HPO_4 = 2AlPO_4 + 2Na_2SO_4 + H_2SO_4$$

It is soluble in potassium and ammonium hydroxide, but not in warm acetic acid. (Distinction from aluminium hydroxide.)

5. **Drop Reaction.**—A solution of aluminium (freed from iron and phosphates by precipitation with ammonia) is made approximately *N* to acid, and equal volumes (*e.g.* 1 drop each)

of 3 *N* ammonium acetate solution and a 0·1 per cent. solution of ammonium aurine tricarboxylate (" aluminon ") are added.

Bright red " lake " colours form in the presence of chromium or of 0·01 mgrm. of aluminium, and the former, although not the latter, is destroyed on addition of a mixture of ammonium carbonate and ammonia. Beryllium gives a similar colour, but other metals do not interfere seriously.

6. Crystal Test.—The solution (which must contain aluminium as chloride) is concentrated, and a drop of a saturated solution of cæsium bisulphate added. In the cold, transparent well-formed octahedra of cæsium alum result (Fig. 14, p. 139), but if the solution is hot dendrites will be observed (sensitiveness 0·1 γ). Sulphates interfere and chromates colour the crystals yellow.

Chromium.

Metallic chromium is very hard, and resembles cast iron. It is fusible only at very high temperatures, and it oxidises slowly on heating in the air. It is readily soluble in sulphuric or hydrochloric acid, but is practically insoluble in nitric acid.

There are three series of chromium compounds: those derived from *chromium sesquioxide*, Cr_2O_3, the **chromic compounds**; those derived from *chromic anhydride*, CrO_3, the **chromates**; and chrom*ous* salts, such as $CrCl_2$. It is only necessary, however, to consider the reactions of the chro*mic* compounds, and of the chromates, because the chromous compounds are very unstable, and readily change into the chromic condition. The dry reactions are the same for both.

In the **chromic salts** $Cr^{\cdots}$ is the cation. The solutions are violet or green (depending upon their concentration and the temperature), and from them **chromium hydroxide**, etc., are precipitated by reagents that precipitate the corresponding **aluminium** compounds. In **chromates**, however, the chromium forms merely part of a complex anion, hence the above statement does not hold unless, as in the case of **ammonium**

sulphide, the reagents first convert the **chromate** to a **chromic salt.**

Chromates and dichromates are yellow and orange in solution, respectively. Their reactions are discussed under the acids (p. 182).

Dry Reactions.—**1.** *Borax Bead.*—Compounds of chromium colour the borax bead an emerald green, and the colour is more intense when the bead is heated in the reducing flame.

2. On mixing a small quantity of a compound of chromium with potassium nitrate and fusion mixture, and heating in a loop of platinum wire, a yellow mass of **sodium and potassium chromate** is obtained. If this is dissolved in a little water, and the yellow solution so obtained is acidified with acetic acid, and then a little silver nitrate added, a red precipitate of silver chromate is produced.

(*a*) $Cr_2O_3 + 3KNO_3 + 2Na_2CO_3 = 2Na_2CrO_4 + 3KNO_2 + 2CO_2$

(*b*) $Na_2CrO_4 + 2AgNO_3 = Ag_2CrO_4 + 2NaNO_3$

Chromic Compounds.

Use a solution of **chrome alum,** or any soluble **chromic** salt.

***1. Ammonium hydroxide** gives a bluish or whitish-green gelatinous precipitate of **chromic hydroxide,** slightly soluble in excess of the reagent, the solution becoming a bluish-pink. From this solution the hydroxide is completely precipitated by boiling.

$$CrCl_3 + 3NH_4OH = Cr(OH)_3 + 3NH_4Cl$$

***2. Sodium** or **potassium hydroxide** produces the same precipitate, soluble in excess to give a bright green solution of **sodium chromite.** The hydroxide is reprecipitated by a large excess of water, the precipitation being complete on boiling. The reaction is therefore reversible.

(*a*) $Cr_2(SO_4)_3 + 6NaOH = 2Cr(OH)_3 + 3Na_2SO_4$

(*b*) $Cr(OH)_3 + 3NaOH \rightleftharpoons Cr(ONa)_3 + 3H_2O$

The presence of non-volatile organic compounds interferes with or entirely prevents the precipitation of chromic hydroxide.

3. Ammonium sulphide gives the same precipitate as (1) and (2), insoluble in excess. (*Cf.* § 3, p. 88.)

$$Cr_2(SO_4)_3+3(NH_4)_2S+6H_2O=2Cr(OH)_3+3(NH_4)_2SO_4+3H_2S$$

4. On adding **sodium peroxide to a cold** solution of a chromic salt, and boiling till effervescence ceases, the chromic salt is oxidised, **sodium chromate** being produced. The colour of the solution changes from green or purple to yellow.

$$2Cr(OH)_3 + 3Na_2O_2 = 2Na_2CrO_4 + 2NaOH + 2H_2O$$

5. Chlorine or **bromine water,** added to a cold solution of a chromic salt which has previously been rendered strongly alkaline with sodium or potassium hydroxide, also oxidises it to a chromate on boiling. In this case the chlorine or bromine is first converted into an alkali hypochlorite, or hypobromite, which then oxidises the chromic salt. (Hypochlorites and hypobromites are *not* produced in *hot* solutions.)

(*a*) $$Br_2+2NaOH=NaOBr+NaBr+H_2O$$

(*b*) $$2Cr(OH)_3+3NaOBr+4NaOH=2Na_2CrO_4+3NaBr+5H_2O$$

If this solution is acidified with sulphuric acid, and boiled till no more bromine is evolved, it may be tested for a chromate with **hydrogen peroxide** (§ 7, p. 184).

When analysing a substance containing a chromate, it becomes reduced to a chromic salt by the action of hydrogen sulphide; the chromium is therefore precipitated in the **iron group.**

6. Drop Reactions.—If a chromate is made slightly acid with hydrochloric acid, and a drop of a 0·2 per cent. solution of diphenyl carbazide in 10 per cent. acetic acid is added, a violet colour results, even in the presence of aluminium and nitrates (sensitiveness 0·4 γ). Certain other oxidising agents give the same reaction, but that from ferric salts is inhibited by the presence of the acid.

Other chromium compounds should first be oxidised to chromates by addition of a drop each of bromine water and of sodium hydroxide, excess of the former being then removed by addition of drops of phenol and sulphuric acid.

7. Crystal Test.—In the presence of nitric acid (which forms a chromate) silver nitrate produces yellow red prismatic crystals of silver dichromate (sensitiveness 0·4 γ).

Iron.

Metallic iron dissolves readily in acids, passing first into the ferr*ous* state with hydrochloric or sulphuric acid, but into the ferr*ic* condition with nitric acid. Ferr*ous* salts are readily converted into fer*ric* salts by oxidation with nitric acid. When ferrous oxide is dissolved in hydrochloric acid, ferrous chloride is first produced.

$$FeO + 2HCl = FeCl_2 + H_2O$$

Whereas when ferric oxide is dissolved, ferric chloride is produced.

$$O\begin{cases} Fe = O \\ Fe = O \end{cases} + 6HCl = 2FeCl_3 + 3H_2O$$

Dry Reactions.—1. *Blowpipe Test.*—Iron compounds yield a black magnetic residue.

2. *Match Test.*—A black magnetic powder is obtained. If this powder is placed on a filter paper and moistened with dilute hydrochloric acid it dissolves, leaving a yellow stain, which, on being moistened with a drop of **potassium ferrocyanide,** turns dark blue.

3. *Borax Bead.*—In the reducing flame a bottle-green bead is produced. In the oxidising flame the bead is dark yellow while hot, light yellow when cold.

Ferrous Iron.

Reactions in Solution.—Use a fresh solution of **ferrous sulphate** or ferrous ammonium sulphate.

*1. **Ammonium sulphide** gives a black precipitate of **ferr*ous* sulphide,** soluble in dilute mineral acids. Moist ferr*ous* sulphide when in contact with air gradually becomes reddish-brown, owing to oxidation.

$$FeSO_4 + (NH_4)_2S = FeS + (NH_4)_2SO_4$$

*2. **Sodium, potassium,** or **ammonium hydroxide** produces a voluminous greenish-white precipitate of **ferr*ous* hydroxide,** which quickly absorbs oxygen from the air, turning first green and finally brown, owing to conversion into **ferr*ic* hydroxide.**

$$FeSO_4 + 2NH_4OH = Fe(OH)_2 + (NH_4)_2SO_4$$

*3. **Potassium ferrocyanide** gives a white precipitate of **potassium ferrous-ferrocyanide,** which rapidly turns blue owing to oxidation. Ferrous salts usually contain traces of ferric salts; therefore the precipitate is rarely white, but generally light blue.

$$FeSO_4 + K_4Fe(CN)_6 = K_2Fe[Fe(CN)_6] + K_2SO_4$$

*4. **Potassium ferricyanide** forms a deep blue precipitate of **ferr*ous*-ferricyanide** (Turnbull's blue). In very dilute solutions only a blue coloration is produced.

$$3FeSO_4 + 2K_3Fe(CN)_6 = Fe_3[Fe(CN)_6]_2 + 3K_2SO_4$$

Turnbull's blue is decomposed by sodium or potassium hydroxide, **ferrous hydroxide** and an alkali ferricyanide being produced. Only the iron which is present as the cation is precipitated as ferrous hydrate; that in the complex anion $Fe(CN)_6'''$ is unaffected.

$$Fe_3[Fe(CN)_6]_2 + 6KOH = 2K_3Fe(CN)_6 + 3Fe(OH)_2$$

5. Drop Reactions.—(*a*) A solution of α-nitroso-β-naphthol added to neutral or slightly ammoniacal solutions of ferrous iron containing sodium acetate produces a green colour. (*b*) Dimethyl glyoxime (see Nickel, p. 103) gives a red colour if tartaric acid is present initially, and ammonia is added finally.

Both these colours change owing to the rapid oxidation of the iron.

Ferric Iron.

Use a solution of **ferric chloride.**

***1. Ammonium sulphide** precipitates black **ferrous sulphide,** along with sulphur.

$$2FeCl_3 + 3(NH_4)_2S = 2FeS + 6NH_4Cl + S$$

***2. Sodium, potassium,** or **ammonium hydroxide** gives a reddish-brown gelatinous precipitate of **ferric hydroxide,** soluble in dilute acids (the presence of many organic compounds, such as tartrates and citrates, hinders or prevents precipitation).

$$FeCl_3 + 3NH_4OH = Fe(OH)_3 + 3NH_4Cl$$

***3. Potassium ferrocyanide** produces a deep-blue precipitate of ferric-ferrocyanide (Prussian blue), $Fe_4[Fe(CN)_6]_3$. It is insoluble in hydrochloric acid, but is soluble in oxalic acid, forming a blue solution (blue ink), but is decomposed by caustic alkalis, with separation of **ferric hydroxide.** The iron in the **cation** alone is precipitated as ferric hydrate, that in the complex anion not being acted upon.

$$Fe_4[Fe(CN)_6]_3 + 12KOH = 4Fe(OH)_3 + 3K_4Fe(CN)_6$$

4. Potassium ferricyanide gives no precipitate, but the colour of the solution becomes brown, because the ferric ferricyanide produced is soluble in water, and is only slightly ionised.

$$Fe(CN)_6''' + Fe^{\cdot\cdot\cdot} \rightleftharpoons Fe[Fe(CN)_6]$$

***5. Potassium thiocyanate** gives a most intense blood-red coloration of **ferric thiocyanate.** The coloration is shown even in very dilute solutions, especially if excess of the thiocyanate and a little hydrochloric acid are added.

$$FeCl_3 + 3KCNS = Fe(CNS)_3 + 3KCl$$

Ferric thiocyanate dissolves in ether or amyl alcohol, and is not decolorised by dilute hydrochloric acid (distinction from the red coloration produced with ferrous salts by acetates and formates). Mercuric chloride or rochelle salt (potassium sodium tartrate), however, destroys the colour, owing in the latter case to the formation of unionised ferric tartrate and the production of strongly ionised alkali thiocyanates.

$$2Fe(CNS)_3+3C_4H_4O_6NaK=Fe_2(C_4H_4O_6)_3+3NaCNS+3KCNS$$

Although, as already stated (p. 21), ferric thiocyanate is only very slightly ionised in solution—hence its red coloration—ferric tartrate is still less ionised; therefore, when the two solutions are brought together, the $Fe^{\cdot\cdot\cdot}$ ions unite with the tartrate $C_4H_4O_6''$ ions to form unionised ferric tartrate.† Equilibrium is thus disturbed, and a further quantity of the ferric thiocyanate becomes ionised. This process goes on until the whole of the ferric thiocyanate has become converted into ferric tartrate. The same reasoning applies to the action of the mercuric chloride, mercuric thiocyanate being less ionised than ferric thiocyanate. The colour reaction is more intense in presence of excess of potassium thiocyanate, as this tends to prevent ionisation of the ferric thiocyanate.

6. Alkali acetates produce a red to reddish-brown coloration from neutral salts; on boiling, the iron is completely precipitated as a basic acetate. (The precipitation does not take place in presence of many organic acids or of poly-alcohols.)

(*a*) $$FeCl_3+3CH_3COOK=\underset{\text{Dark brown colour}}{(CH_3COO)_3Fe}+3KCl$$

(*b*) $$(CH_3COO)_3Fe+2H.OH=CH_3COO.Fe(OH)_2+2CH_3COOH$$

† This is probably a basic compound, and very likely consists of colloidal ferric hydroxide and basic ferric tartrate.

7. Drop Reactions.—(*a*) Drops of solutions of a ferric (or ferrous) salt and thioglycollic acid are mixed, and a trace of ammonia is added, when a purple colour is produced (sensitiveness 0·5 γ).

(*b*) α-Nitroso-β-naphthol produces a brown colour in slightly acid solutions. (*Cf.* Ferrous salts.)

(*c*) Cupferron (p. 114) produces a red colour.

(*d*) Alloxantine gives a blue colour in the presence of dilute alkali.

Tests Nos. 3, 4, and 5 given above also make excellent drop reactions. With the exception of No. 7 (*a*), they are all selective for ferric salts in the presence of ferrous salts.

Reduction of Ferric Compounds to the Ferrous State.—If a solution of a ferric salt is warmed with zinc and hydrochloric acid, the nascent hydrogen evolved reduces it to a ferrous salt.

$$2FeCl_3 + 2H = 2FeCl_2 + 2HCl$$

The same effect is produced on warming with sulphurous acid.

$$2FeCl_3 + 2H_2O + SO_2 = 2FeCl_2 + 2HCl + H_2SO_4$$

Reduction is also effected by H_2S, with accompanying precipitation of sulphur.

$$2FeCl_3 + H_2S = 2FeCl_2 + S + 2HCl$$

If the reduction is complete, the iron salt no longer gives the reactions of the ferric ion, but will answer to those for the ferrous ion.

Detection of Ferrous Iron in Presence of Ferric Iron.—
1. Add to the solution of the mixed salts a solution of potassium thiocyanate—an intense red coloration, showing the presence of ferric iron, is produced. Now add a few crystals of rochelle salt and warm gently, and the colour changes to a light brown. On addition of a solution of potassium ferricyanide a deep blue coloration or precipitate is produced, indicating the presence of a ferrous salt.

2. The drop reactions given under ferrous and ferric iron are all selective for the ion concerned, with the exceptions of thioglycollic acid, which reacts with either.

Manganese.

Metallic manganese resembles iron very much in appearance, and is soluble in dilute mineral acids. It forms several series of compounds in two of which the cation is divalent and trivalent, respectively; *viz.* stable **manganous** salts, derived from basic **manganous oxide,** MnO; and unstable **manganic** salts, from basic **manganese sesquioxide,** Mn_2O_3. There are also the **manganates** and **permanganates,** in which Mn is merely part of the MnO_4 anion, being divalent in the **manganates,** but monovalent in the **permanganates.**

Dry Reactions.—1. If a small quantity of a manganese compound is mixed with fusion mixture, and is then taken up upon a small loop of platinum wire, and held in the oxidising flame of the Bunsen burner until completely fused, the resulting mass will be a deep green colour, owing to the formation of an alkali **manganate.**

$$NnO_2 + Na_2CO_3 + O = Na_2MnO_4 + CO_2$$

It is sometimes recommended to add a little nitre as well as fusion mixture in this case. The following reaction, however, does not then always show to advantage, because of the reducing action of the potassium nitrite formed.

If the fused mass is dissolved in about 1 c.c. of water, and acidified with dilute sulphuric acid, a rose-red coloration will be imparted to the solution, owing to the oxidation of the **sodium manganate** to **permanganate.** The oxidation takes place without the addition of acid on allowing the solution to stand in contact with air for a short time. In the latter case, however, a brown precipitate of $MnO(OH)_2$ is produced at the same time.

$$3Na_2MnO_4 + 3H_2O = 2NaMnO_4 + MnO(OH)_2 + 4NaOH$$

2. *Borax Bead.*—Manganese compounds, when heated in the oxidising flame, colour the borax or microcosmic bead an amethyst purple. The bead is colourless in the reducing flame.

Reactions in Solution.—Use a solution of **manganese chloride** or **sulphate.**

***1. Ammonium sulphide** gives a flesh-coloured precipitate of **manganese sulphide.** In very dilute solutions the precipitate has a yellowish-white appearance. It is readily soluble in mineral acids, and in acetic acid (distinction from zinc).

$$MnCl_2 + (NH_4)_2S = MnS + 2NH_4Cl$$

***2. Sodium** or **potassium hydroxide** produces a white precipitate of **manganous hydroxide,** which rapidly turns brown in the air, owing to formation of **manganic hydroxide,** $MnO(OH)_2$, by oxidation.

$$(1) \quad MnCl_2 + 2KOH = Mn(OH)_2 + 2KCl$$

$$(2) \quad Mn\begin{cases} OH \\ OH \end{cases} + O = Mn\begin{cases} OH\dagger \\ =O \\ OH \end{cases}$$

***3. Ammonium hydroxide** forms the same precipitate. In the presence of ammonium chloride no precipitation takes place, because although ammonium hydroxide is ordinarily sufficiently ionised to precipitate **manganese hydroxide,** in the presence of a strongly dissociated ammonium salt ionisation is so slight that there are not enough OH' ions present to precipitate $Mn(OH)_2$. On exposure to air, a brown precipitate of **manganic hydroxide** gradually separates out.

***4. Permanganate Reaction.**—(*a*) Ammonium persulphate is added to a hot solution of a manganese salt in dilute nitric acid. Normally, hydrated manganese dioxide is produced by oxidation, but if a little silver nitrate is present

† This is acidic in character, and reacts with the basic manganous hydroxide to form salts—*manganites.*

as catalyst, the oxidation proceeds to the permanganate stage, and a pink colour results.

$$2MnCl_2 + 5(NH_4)_2S_2O_8 + 8H_2O = 5(NH_4)_2SO_4 + 2HMnO_4 + 5H_2SO_4 + 4HCl$$

(*b*) See Drop Reaction, § 5 (*b*).

5. Drop Reactions.—(*a*) The precipitate produced from a drop each of manganese solution and potassium hydroxide is isolated on a watch-glass by drawing up the liquid on a strip of filter paper, and a drop of benzidine acetate is added followed by a drop of dilute acetic acid. A blue colour results.

(*b*) The pink colour of potassium permanganate is produced on mixing, in order, drops of manganese solution, phosphoric acid and water, and then adding a crystal of potassium periodate (sensitiveness 0·5 γ). Reaction No. 4 (*a*) may be used similarly.

NOTE.—As permanganates are reduced by H_2S, SO_2, etc., they will, after treatment with such reducing agents, give the same reactions as manganous salts. For reactions of permanganic acid, see p. 185.

Zinc.

Perfectly pure zinc is not readily soluble in acids, but as usually obtained it is readily soluble. The pure metal dissolves in dilute acids especially after the addition of a drop or two of copper sulphate or of cadmium sulphate solution. It dissolves in boiling alkalis, with evolution of hydrogen and formation of an alkali zincate.

$$Zn + 2KOH = K_2ZnO_2 + H_2$$

Dry Reactions.—**1.** *Blowpipe Test.*—When heated on charcoal with fusion mixture, compounds of zinc are reduced to the metallic state. Owing, however, to the volatility of the metal, no bead is obtained; but on the charcoal an incrustation of the oxide is formed, which is yellow while hot,

and white when cool. If the oxide is moistened with a drop of cobalt nitrate, and again heated, a green-coloured compound is produced.

2. *Filter Ash Test* (p. 11).—The ash is tinged green.

3. *Borax Bead.*—This is yellowish while hot, but colourless on cooling; if a large quantity of zinc salt has been employed the bead is often opaque.

Reactions in Solution.—Use a solution of **zinc sulphate.**

*1. **Ammonium sulphide** gives a white precipitate of **zinc sulphide,** soluble in mineral acids, insoluble in acetic acid and sodium acetate (distinction from manganese); if iron is present even in traces, it is dark in colour.

$$ZnSO_4 + (NH_4)_2S = ZnS + (NH_4)_2SO_4$$

*2. **Sodium** or **potassium hydroxide** produces a white gelatinous precipitate of **zinc hydroxide,** soluble in excess with formation of an alkali zincate, from which ammonium sulphide precipitates zinc sulphide.

(*a*) $ZnSO_4 + 2NaOH = Zn(OH)_2 + Na_2SO_4$

(*b*) $Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O$

3. **Ammonium hydroxide** gives the same precipitate, soluble in excess, but no precipitation takes place in presence of ammonium salts.

*4. **Potassium ferrocyanide** forms a white gelatinous precipitate of **zinc ferrocyanide,** insoluble in acetic acid. (Compare § 3, p. 93.)

$$2ZnSO_4 + K_4Fe(CN)_6 = Zn_2Fe(CN)_6 + 2K_2SO_4$$

5. **Sodium carbonate** produces a bulky white precipitate of a basic zinc carbonate.

$$5ZnSO_4+5Na_2CO_3+3H_2O=2ZnCO_3,\ 3Zn(OH)_2+5Na_2SO_4 +3CO_2$$

6. **Drop Reaction.**—A drop of a 0·002 per cent. solution of diphenylthiocarbazone in carbon tetrachloride is added to a drop of the neutral zinc solution in a micro test-tube. On

shaking, the green colour of the former layer turns red (sensitiveness 1 γ).

7. Crystal Test.—The mercury thiocyanate reagent (p. 371) gives characteristic feathery radiating tufts of rhombic crystals (Fig. 15, p. 139), the sensitiveness being 0·1 γ.

Nickel.

Nickel is a very hard metal, which takes on a bright polish when burnished. It is readily soluble in nitric acid, less soluble in sulphuric or hydrochloric acid. The salts of nickel are green in solution or when crystalline, and usually yellow when anhydrous. Nickel forms many alloys, most of which are soluble in nitric acid. The oxides are green **nickelous oxide** (NiO) and dark brown **nickel oxide** (Ni_2O_3). The latter is a peroxide and does not form salts, and both are soluble in acids to give salts of divalent (*nickelous*) nickel.

Dry Reactions.—1. *Blowpipe Test.*—Nickel compounds are reduced to a black powder of metallic nickel, which is magnetic.

2. *Match Test.*—Black magnetic powder obtained.

3. *Borax Bead.*—In the oxidising flame compounds of nickel give a yellowish-brown bead; in the reducing flame it is opaque and grey, owing to particles of metallic nickel.

Reactions in Solution.—Use a solution of **nickel chloride** or **sulphate.**

***1. Ammonium sulphide** gives a black precipitate of **nickel sulphide** which is slightly soluble in ammonia; therefore, on filtering a strong ammoniacal solution, the filtrate is often coloured brown. If this solution is acidified with acetic acid and gently warmed, the nickel sulphide is completely precipitated.

$$NiCl_2 + (NH_4)_2S = NiS + 2NH_4Cl$$

Nickel sulphide is practically insoluble in dilute hydrochloric acid, but is readily dissolved on warming with hydrochloric

acid containing a crystal of potassium chlorate, or in aqua regia.

*2. **Sodium** or **potassium hydroxide** produces a light green gelatinous precipitate of **nickelous hydroxide**, insoluble in excess, but readily soluble in acids.

$$NiCl_2 + 2KOH = Ni(OH)_2 + 2KCl$$

On addition of oxidising agents such as hypochlorites, hydrogen peroxide, etc., the nickelous hydroxide is oxidised to nickelic hydroxide.

$$2Ni(OH)_2 + NaOBr + H_2O = 2Ni(OH)_3 + NaBr$$

3. **Ammonium hydroxide** gives a voluminous greenish precipitate of basic sulphate which is readily soluble in excess, a deep blue solution of a complex nickel ammonium salt $[Ni(NH_3)_6SO_4]$ being formed.

$$2NiSO_4 + 2NH_4OH = \begin{matrix} Ni-OH \\ >SO_4 \\ Ni-OH \end{matrix} + (NH_4)_2SO_4$$

*4. **Potassium cyanide** produces a green precipitate of **nickel cyanide.**

$$NiCl_2 + 2KCN = Ni(CN)_2 + 2KCl$$

It is soluble in excess of potassium cyanide, forming a so-called double cyanide of potassium and nickel.

$$Ni(CN)_2 + 2KCN = K_2Ni(CN)_4$$

From this solution nickel cyanide is precipitated by addition of acids. Hydrogen sulphide produces no precipitate from this solution, because the nickel is in the stable complex anion $Ni(CN)_4''$.

5. It is, however, readily decomposed by chlorine or bromine and by hypochlorites.

$$K_2Ni(CN)_4 + 4Br_2 = NiBr_2 + 2KBr + 4CNBr$$

This decomposition is one of great importance, because it is used to separate nickel from cobalt (see p. 106). The potassium cobalticyanide is much more stable than the potassium

nickelocyanide, and is not decomposed under similar conditions. Add to a solution of a nickel salt *just sufficient* potassium cyanide to dissolve the precipitate at first produced. Now add a slight excess of caustic soda (*cf.* § 2, p. 102), and then sufficient **bromine water** to give a permanent colour to the solution. On gently warming, a black precipitate of **nickelic hydroxide** will be thrown down. The **nickelic hydroxide** is precipitated owing to the complete decomposition of the molecule $K_2Ni(CN)_4$ (distinction from **cobalt**).

$$2K_2Ni(CN)_4 + NaOBr + 5H_2O = 2Ni(OH)_3 + NaBr + 4KCN + 4HCN$$

If a large excess of potassium cyanide or caustic soda is present the reaction does not take place very readily.

6. Drop Reaction.—A 1 per cent. solution of dimethyl glyoxime in alcohol is added to a warm drop of the nickel salt, followed, after cooling, by sufficient ammonia to make the mixture just alkaline. A brilliant red colour or precipitate results (sensitiveness 0·3 γ). Ferrous salts give a red colour only. This reaction may be used in the presence of cobalt (see below).

Nickel in Cobalt Salts.—Ammonia is added until a clear solution is obtained, and 2 c.c. of hydrogen peroxide are added to this, excess being removed by boiling. A 1 per cent. solution of dimethylglyoxime in alcohol is then added, and the liquid is boiled, when a red precipitate or colour results. The reaction is very sensitive, even when a relatively large amount of cobalt is present.

Cobalt.

Metallic cobalt is very similar to nickel. Nitric acid is the best solvent. The solutions of cobalt salts are red; the anhydrous salts, however, are usually blue. But anhydrous cobalt sulphate is red, both in the anhydrous state and in aqueous solution. The three oxides of cobalt are, **cobaltous**

oxide, CoO; **cobaltous-cobaltic oxide,** Co_3O_4; and **cobaltic oxide,** Co_2O_3. In all cases their acids form cobalt*ous* salts (*e.g.* $CoCl_2$), the cobalt*ic* compounds (containing trivalent cobalt) being restricted to com^lex salts (see § 5).

Dry Reactions.—1. *Blowpipe Test.*—Cobalt compounds are reduced to a black metallic magnetic powder.

2. *Match Test.*—A black magnetic powder obtained.

3. *Borax Bead.*—In both the oxidising and reducing flame the bead is coloured a beautiful sapphire blue.

Reactions in Solution.—Use a solution of **cobalt chloride** or **nitrate.**

1. **Ammonium sulphide** produces a black precipitate of **cobalt sulphide,** which is insoluble in excess of ammonium sulphide, and in dilute acids. It is readily soluble in aqua regia, or in hydrochloric acid, to which a little potassium chlorate has been added.

$$Co(NO_3)_2 + (NH_4)_2S = CoS + 2NH_4NO_3$$

*2. **Potassium** or **sodium hydroxide** gives a bluish precipitate of basic chloride.

$$(a) \quad CoCl_2 + NaOH = Co(OH)Cl + NaCl$$
$$(b) \quad Co(OH)Cl + NaOH = Co(OH)_2 + NaCl$$

This on boiling turns light red, being converted into **cobaltous hydroxide,** $Co(OH)_2$, which, owing to further oxidation, rapidly turns to brown cobaltic hydroxide.

$$2Co(OH)_2 + O + H.OH = 2Co(OH)_3$$

*3. **Ammonium hydroxide** produces the same precipitate. It dissolves readily in excess of the reagent, forming a brown solution which turns purple on boiling, but owing to oxidation, it rapidly becomes a permanent brown.

*4. **Potassium cyanide** forms a buff-coloured precipitate of **cobaltous cyanide.**

$$Co(NO_3)_2 + 2KCN = Co(CN)_2 + 2KNO_3$$

It dissolves readily in excess of the precipitant, being converted into **potassium cobaltocyanide.**

$$Co(CN)_2 + 4KCN = K_4Co(CN)_6$$

This salt is very readily oxidised to **potassium cobalticyanide,** the conversion taking place even on boiling with water alone, but more rapidly if a trace of acid or an oxidising agent is present.

$$2K_4Co(CN)_6 + O + H_2O = 2K_3Co(CN)_6 + 2KOH$$

It should be noticed that **potassium cobaltocyanide** corresponds with **potassium ferrocyanide,** and the **cobalticyanide** with **ferricyanide.** Caustic alkalis and bromine water do not precipitate the hydroxide from this solution (cf. Nickel), because the potassium cobalticyanide is a very stable substance, and so long as the cobalt remains in the complex anion $Co(CN)_6'''$, it will not be precipitated by the ordinary reagents for the ion $Co^{\cdot\cdot}$.

***5. Potassium nitrite,** when added to neutral solutions of cobalt salts which have been strongly acidified with acetic acid, produces a brilliant yellow precipitate of **potassium cobaltinitrite.** Probably potassium cobaltonitrite is first formed, and then becomes oxidised by the nitrous acid set free on the addition of the acetic acid.

(i) $CoCl_2 + 6KNO_2 = K_4Co(NO_2)_6 + 2KCl$

(ii) $K_4Co(NO_2)_6 + HNO_2 + CH_3 . COOH$
$= K_3Co(NO_2)_6 + CH_3 . COOK + H_2O + NO$

This reaction is also used for the separation of nickel and cobalt (p. 106).

***6. Ammonium thiocyanate.**—When a concentrated solution of ammonium thiocyanate is added to a cobaltous solution a brilliant blue coloration due to the formation of ammonium cobaltous thiocyanate is produced.

(i) $Co(NO_3)_2 + 2NH_4CNS = Co(CNS)_2 + 2NH_4NO_3$

(ii) $Co(CNS)_2 + 2NH_4CNS \rightleftharpoons (NH_4)_2[Co(CNS)_4]$

If the solution is diluted the blue colour vanishes, and the reaction is therefore reversible. The test can be made extremely delicate by adding a mixture of equal volumes of amyl alcohol and ether before the ammonium thiocyanate. On shaking the blue coloration is imparted to the alcohol-ether layer, which floats upon the surface of the aqueous solution. The reaction can be employed in presence of nickel, which gives no coloration. The merest trace of cobalt can be detected in this manner.

7. Drop Reaction.—One drop of the neutral or faintly acid solution is added to a drop of a 0·05 per cent. solution of α-nitroso-β-naphthol in 50 per cent. acetic acid. A purple red colour results (sensitiveness 0·01 γ) even in the presence of nickel.

8. Crystal Test.—The warm mercury thiocyanate reagent (p. 371) gives characteristic radiating groups of blue, pointed, rhombic crystals (Fig. 16, p. 139). The sensitiveness is 0·05 γ, and nickel and manganese do not interfere.

Separation of Nickel and Cobalt.—Owing to the similarity of the reactions of these two metals their separation is very difficult. They may, however, be separated (i) by taking advantage of their different behaviour with **potassium cyanide**, and (ii) by the behaviour of cobalt with **potassium nitrite.**

(i) To a neutral solution containing nickel and cobalt, add potassium cyanide until the precipitate first formed is just redissolved. Now add two or three drops of acetic acid, and boil in the draught cupboard for three or four minutes (any precipitate which forms should be filtered off and neglected). *Cool* the solution; make slightly alkaline with caustic soda, and add bromine water till a permanent brown coloration is produced. Warm; a black precipitate of **nickel hydroxide** will be formed; filter this off, and, after washing, confirm nickel by means of the borax bead. The cobalt is obtained by evaporating the solution to dryness and testing with the borax bead, a sapphire-blue colour showing the presence of cobalt.

(ii) Render the neutral solution strongly acid with acetic acid, and add a solution of **potassium nitrite.** Add to the mixture about one-third its volume of alcohol, and shake well. Potassium cobaltinitrite will separate out as a golden-yellow powder. Allow to stand about a quarter of an hour, or, if the solution is dilute, for an hour or two, and filter off. The nickel may be precipitated from the solution by means of sodium hydroxide, and confirmed by means of the borax bead.

Cerium.

Cerium forms two classes of compounds—the **cerous,** derived from the sesquioxide Ce_2O_3; and the **ceric,** derived from the dioxide CeO_2. The ceric salts as a rule are not very stable.

Dry Reactions.—**1.** *Blowpipe Test.*—When strongly heated on charcoal an orange or reddish-brown mass of **cerium dioxide** is obtained.

2. *Borax Bead.*—In the oxidising flame the bead is brownish-green while hot, bluish-green on cooling. In the reducing flame the bead is colourless.

Reactions in Solutions.—Use a solution of **cerium nitrate.**

***1. Ammonium sulphide** or **hydroxide** gives a white precipitate of **cerous hydroxide.**

$$CeCl_3 + 3NH_4OH = Ce(OH)_3 + 3NH_4Cl$$

2. Potassium or **sodium hydroxide** produces the same precipitate. Addition of oxidising agents, such as chlorine water or hydrogen peroxide, converts cerous hydroxide into yellow **ceric hydroxide.**

***3. Sodium peroxide** added to a solution of the cerous salt produces a brown gelatinous precipitate of **ceric hydroxide,** which rather resembles ferric hydroxide in appearance.

$$2Ce(NO_3)_3 + 6NaOH + H_2O_2 = 2Ce(OH)_4 + 6NaNO_3$$

*4. **Ammonium oxalate** or **oxalic acid** gives a white precipitate of **cerium oxalate,** which is insoluble in excess of oxalic acid.

$$2CeCl_3 + 3H_2C_2O_4 = Ce_2(C_2O_4)_3 + 6HCl$$

5. **Drop Reactions.**—(*a*) Ceric salts give a blue colour with a 2 per cent. solution of benzidine in 1 per cent. hydrochloric acid.

(*b*) The reaction for hydrogen peroxide described in § 6, p. 192, may also be applied to cerium.

Zirconium.

Zirconium is obtained as a black powder or in hard, brittle lustrous scales. It is only slightly soluble in acids, and it forms one oxide, ZrO_2.

Reactions in Solution.—Use a solution of zirconium nitrate.

1. **Alkalis.**—Sodium or potassium hydroxide produces in the cold a slimy white precipitate of zirconium hydroxide, which is insoluble in excess (distinction from beryllium and aluminium) and soluble in acids. Tartaric acid prevents precipitation (distinction from iron, but not from aluminium, or beryllium).

Ammonia produces a slimy white precipitate insoluble in excess.

2. **Hydrogen peroxide** produces a white precipitate of zirconium peroxide in acid solutions (distinction from titanium), and this liberates chlorine from hydrochloric acid in the warm.

3. **Cupferron** (see p. 114) produces a curdy white precipitate when treated by the method described for titanium (§ 8, p. 114). It may be used for the separation from aluminium or iron.

4. **Drop Reaction.**—The reagent is a solution of alizarin in alcohol to which hydrochloric acid has been added until the colour is yellow. One drop is added to a neutral solution of zirconium. The mixture is boiled in a micro-crucible, and

a drop of *N* hydrochloric acid is added. A red-blue lake is produced. Phosphates, sulphates, and tungstates interfere.

Gallium.

Gallium is a hard white metal, and occurs in many localities in small quantities. It is soluble in warm acids or alkalis with evolution of hydrogen, and it forms divalent (gallous) and trivalent (gallic) salts.

Reactions in Solution.—Use gallic chloride, $GaCl_3$.

1. **Alkalis** give a white precipitate of the hydroxide $Ga(OH)_3$, soluble in excess. Ammonia produces no precipitate in the presence of tartaric acid.

2. **Potassium ferrocyanide** gives a white or pale blue precipitate of gallium ferrocyanide.

Separation.—(*a*) Ether removes gallium trichloride in the presence of hydrochloric acid. *Iron* and *thallium* are also removed unless previously reduced by shaking with mercury.

(*b*) *Indium* is precipitated with excess of 5 per cent. sodium carbonate solution, and gallium is removed from the filtrate by precipitation with camphoric acid.

(*c*) *Thallium* (as sulphate) and *iron* are reduced with sulphur dioxide, gallium is precipitated as in (*b*), and the thallium is precipitated from the filtrate by potassium chromate.

Beryllium (Glucinum).

This is a divalent metal very similar in its reactions to aluminium, and it dissolves in warm acids (except strong nitric acid) or alkalis, with evolution of hydrogen. It forms a white oxide, BeO.

Reactions in Solution.—Use beryllium chloride or sulphate.

1. **Alkalis** produce similar precipitates as with aluminium. Ammonium carbonate, however, produces a precipitate which is soluble in excess (distinction from aluminium).

2. Potassium sulphate produces the double salt $K_2Be(SO_4)_2$, $2H_2O$, which is soluble in a strong solution of potassium sulphate (distinction from cerium and lanthanum).

3. Drop Reaction.—A filter paper is spotted with a drop of a 0·05 per cent. solution of quinalizarin in 0·25 *N* sodium hydroxide ; a drop of a solution of beryllium containing sodium hydroxide produces a blue spot in the violet colour of the reagent (sensitiveness 0·2 γ). Zirconium and magnesium react similarly, but treatment of the spot with bromine water removes the colour due to the last. Aluminium does not react.

4. Separation.—(*a*) *From Aluminium.*—(i) Beryllium chloride is selectively soluble in a mixture of equal volumes of ether and hydrochloric acid. (ii) A solution of the freshly-precipitated hydroxides in glacial acetic acid is extracted with chloroform, when beryllium only [as BeO, $3Be(C_2H_3O_2)_2$] is removed.

(*b*) *From Uranium.*—Basic beryllium acetate is insoluble in chloroform, whereas the corresponding salt of uranium is not.

Lanthanum.

Reactions in Solution.—Use a solution of lanthanum nitrate, $La(NO_3)_3$.

1. All **alkalis** produce white precipitates, usually of the hydroxide, $La(OH)_3$. Tartaric acid prevents precipitation by ammonia (distinction from yttrium). The precipitate with ammonium carbonate is soluble in excess of reagent (distinction from aluminium).

2. Solid **iodine** produces a blue colour similar to that of starch iodide (p. 146) when mixed with the precipitate produced on adding ammonia to an acetic acid solution containing lanthanum. The precipitate should first be washed, as the colour is destroyed by acid or alkali.

Vanadium.

Vanadium, niobium (columbium), and tantalum form compounds closely related to phosphorus. They also, however, show similarities to iron, chromium, and tungsten.

Dry Reactions.—*Microcosmic bead*, yellow in oxidising flame, beautiful green in the reducing flame.

Reactions in Solution.—Use a solution of sodium vanadate, $Na_4V_2O_7$.

1. **Hydrogen sulphide** gives no precipitate in acid solutions, but the solution becomes blue owing to reduction of the vanadic acid to a divanadyl compound.

$$V_2O_5 + H_2S = 2VO_2 + H_2O + S$$

2. **Ammonium sulphide** causes the solution to turn brown, but no precipitate is produced owing to the formation of thiosalts; on acidifying a brown precipitate of **vanadic sulphide**, V_2S_5, is produced. The sulphide is soluble in alkalis, alkali carbonates and alkali sulphides.

$$(NH_4)_4V_2S_7 + 4HCl = 4NH_4Cl + V_2S_5 + 2H_2S$$

The precipitation of the sulphide is not quantitative, as a portion of the vanadate is reduced, so that the solution always has a blue colour.

3. **Ammonium chloride.**—Solid ammonium chloride, when added to a solution of an alkali vanadate, produces a colourless crystalline precipitate of **ammonium vanadate**, sparingly soluble in strong ammonium chloride.

$$Na_4V_2O_7 + 4NH_4Cl = 2NH_4VO_3 + 4NaCl + H_2O + 2NH_3$$

4. **Mercurous nitrate** gives, from neutral solutions, a yellowish precipitate of **mercurous vanadate**, soluble in nitric acid.

$$Na_4V_2O_7 + Hg_2(NO_3)_2 + H_2O = 2HgVO_3 + 2NaNO_3 + 2NaOH$$

5. **Hydrogen peroxide** when added to an acid solution of a vanadate colours the solution reddish-brown. This is a very

delicate test both for vanadium and conversely for hydrogen peroxide. The hydrogen peroxide must not be added in excess as then the reaction is less delicate.

6. **Reducing agents** such as sulphur dioxide, oxalic acid, hydrobromic acid, etc., reduce vanadates to **vanadyl salts**, therefore the solutions become blue on addition of the reducing agent. With hydriodic acid the colour is first blue and then green because the vanadic oxide is reduced to the **sesquioxide**, but the presence of the iodine to a large extent masks the reaction, although the colour is visible even after it has been boiled off.

$$H_3VO_4 + 2HI + 3HCl = VCl_3 + 4H_2O + I_2$$

The addition of Zn, Al, or Mg to acid solutions causes the reduction to be carried still further, and the solution becomes first blue, then green, and finally violet (divalent vanadium).

7. **Separation.**—Add a solution of uranyl acetate and ammonium acetate to a neutral solution of the vanadium salt, when uranyl ammonium vanadate is precipitated.

$$(UO_2)NH_4VO_4,\ H_2O$$

This is very insoluble and may be used to separate vanadium from copper, alkali and alkali earth metals, zinc and manganese.

Titanium.

Oxides, Ti_2O_2, Ti_2O_3, TiO_2, TiO_3.

Ti_2O_2 and Ti_2O_3 form violet-coloured salts which are easily converted into derivatives of TiO_2 by oxidising agents.

The dioxide is most important, and has both acidic and basic properties. The best method to prepare a soluble salt is to fuse with potassium pyrosulphate, or to boil with concentrated sulphuric acid containing potassium bisulphate.

$$TiO_2 + 2K_2S_2O_7 = Ti(SO_4)_2 + 2K_2SO_4$$

Dry Reaction.—*Borax bead*, no coloration in the oxidising flame, but on continued heating in the reducing flame

the bead becomes yellow while hot and violet on cooling. The addition of a trace of stannous chloride causes the colour to appear much more rapidly. The addition of an iron salt produces a brownish or reddish-brown bead.

Wet Reactions.—Use a solution of **titanium sulphate.**

1. Potassium hydroxide gives in the cold a gelatinous precipitate of orthotitanic acid.

$$Ti(SO_4)_2 + 4KOH = Ti(OH)_4 + 2K_2SO_4$$

It is almost insoluble in excess of the hydroxide but readily soluble in mineral acids. When precipitated from hot solutions meta-titanic acid is precipitated which is difficultly soluble in diluted mineral acids.

$$Ti(SO_4)_2 + 4KOH = H_2TiO_3 + 2K_2SO_4 + H_2O$$

On long digestion with concentrated sulphuric or hydrochloric acid it slowly goes into solution.

2. Alkali acetates precipitate the whole of the titanium as metatitanic acid on boiling. The acetate is first produced, but is hydrolysed.

$$Ti(SO_4)_2 + 4CH_3COONa + 3H_2O = H_2TiO_3 + 2Na_2SO_4 + 4CH_3COOH$$

3. Water in excess hydrolyses all titanium salts with precipitation of metatitanic acid; reaction is complete on boiling.

$$TiCl_4 + 3H_2O \rightleftharpoons H_2TiO_3 + 4HCl$$

The separation of titanium from the metals of the iron group depends upon this property. The mixed oxides are fused with potassium bisulphate, the fusion product dissolved in cold water and then boiled.

Tartaric acid and many other organic substances prevent the precipitation, so that when organic substances are present they must first be removed by ignition.

4. Ammonium hydroxide and sulphide and also **barium carbonate** in the cold precipitate orthotitanic acid—readily soluble in acids. From hot solutions the metatitanic acid which is difficultly soluble in acids is precipitated.

$$Ti(SO_4)_2 + 4NH_4OH = Ti(OH)_4 + 2(NH_4)_2SO_4$$
$$Ti(SO_4)_2 + 2(NH_4)_2S + 4H_2O = Ti(OH)_4 + 2H_2S + 2(NH_4)_2SO_4$$
$$Ti(SO_4)_2 + 2BaCO_3 + 2H_2O = Ti(OH)_4 + 2BaSO_4 + 2CO_2$$

5. Sodium phosphate gives from boiling solutions a precipitate of basic titanium phosphate. It is soluble in mineral acids

$$Ti(SO_4)_2 + 2HNa_2PO_4 = Ti(HPO_4)_2 + 2Na_2SO_4$$

and in acetic acid.

6. Hydrogen peroxide.—On adding hydrogen peroxide to a slightly acid solution of titanium sulphate an orange-red colour is produced; with very diluted solutions the colour is yellow. The reaction, which is one of extreme delicacy, depends upon the formation of the trioxide. It is employed as a test for hydrogen peroxide (**Drop Reaction**) and as a test for traces of titanium in rocks (see § 5, p. 191). Vanadic acid produces a similar coloration.

7. Zinc or **tin** when added to acid solutions of titanium salts produces a violet coloration owing to reduction.

$$TiCl_4 + H = TiCl_3 + HCl$$

Sulphur dioxide and hydrogen sulphide do not reduce titanium compounds.

8. Cupferron (a 5 per cent. solution of ammonium nitroso-phenyl-hydroxylamine) is added to an acid solution containing titanium, when a yellow precipitate results. Iron gives a red precipitate and zirconium and copper also react.

9. Separation from iron.—Add about 5 grms. of tartaric acid to 150 c.c. of solution, followed by excess of ammonia and pass hydrogen sulphide. Iron sulphide only is precipitated.

Uranium.

Uranium forms the dioxide UO_2 and the trioxide UO_2O, called **uranyl oxide.** The dioxide (out of contact with air) dissolves in strong acids and forms **uranous salts.**

$$UO_2 + 4HCl = UCl_4 + 2H_2O$$

These salts are very unstable, and on exposure to air rapidly change into **uranyl salts.**

$$UCl_4 + H_2O + O = O_2UCl_2 + 2HCl$$

Uranyl oxide dissolves in acids and forms uranyl salts.

$$UO_2O + H_2SO_4 = O_2USO_4 + H_2O$$

All uranyl salts are coloured either yellow or greenish-yellow, and are mostly soluble in water.

Dry Reactions.—*Borax bead,* yellow in oxidising flame, green in reducing flame.

Reactions in Solution.—Use a solution of **uranium nitrate,** $O_2U(NO_3)_2$, or the acetate $O_2U(CH_3COO)_2$.

1. **Alkali hydroxides** give a yellow precipitate of potassium uranate.

The reaction is rather complicated but probably takes place as follows :—

$$\begin{array}{lcccl} & NO_3 & KOH & & OH & \\ UO_2 & & + & = UO_2 & & + 2KNO_2 \\ & NO_2 & KOH & & OH & \end{array}$$

The hydroxide splits off water and is converted into **uranic acid** by union of two molecules.

$$\begin{array}{llll} & OH & & OH \\ UO_2 & & UO_2 & \\ & OH & = & \\ & O H & & {>}O + H_2O \\ UO_2 & & UO_2 & \\ & OH & & OH \end{array}$$

The uranic acid then combines with the excess of alkali hydroxide and forms a salt.

$$\begin{array}{l} UO_2\diagup OH \\ \quad \rangle O \\ UO_2\diagdown OH \end{array} + \begin{array}{l} KOH \\ \\ KOH \end{array} = \begin{array}{l} UO_2\diagup OK \\ \quad \rangle O \\ UO_2\diagdown OK \end{array} + 2H_2O$$

2. **Ammonium hydroxide** also gives a precipitate of ammonium uranate.

The alkali uranates dissolve in alkali carbonates, especially in ammonium carbonate, with formation of complex salts.

$$\begin{array}{l} UO_2 - ONH_4 \\ \quad >O \\ UO_2 - ONH_4 \end{array} + 6(NH_4)_2CO_3 + 3H_2O$$
$$= 2[UO_2(CO_3)_3](NH_4)_4 + 6NH_4OH$$

Therefore in presence of an alkali carbonate precipitation is either incomplete or fails to take place. Organic acids also prevent precipitation.

3. **Ammonium sulphide** gives a brown precipitate of uranyl sulphide.

$$UO_2(NO_3)_2 + (NH_4)_2S = UO_2S + 2NH_4NO_3$$

It is soluble in dilute acids and in ammonium carbonate.

$$UO_2S + 3(NH_4)_2CO_3 = [UO_2(CO_3)_3](NH_4)_4 + (NH_4)_2S$$

Consequently no precipitate is produced in presence of ammonium carbonate.

4. **Sodium phosphate** gives a whitish-yellow precipitate of uranyl phosphate.

$$UO_2\begin{array}{l}\diagup NO_3 \\ \diagdown NO_3\end{array} + \begin{array}{l} Na\diagdown \\ Na - PO_4 \\ H\diagup \end{array} = \begin{array}{l} UO_2\diagdown \\ \qquad >PO_4 \\ H\diagup \end{array} + 2NaNO_3$$

When ammonium acetate is present, a precipitate of ammonium uranyl phosphate is obtained.

$$Na_2HPO_4 + UO_2(NO_3)_2 + CH_3 . COONH_4 = PO_4\begin{matrix} /\!\!/ UO_2 \\ \diagdown NH_4 \end{matrix}$$

$$+ CH_3 . COOH + 2NaNO_3$$

The precipitates are soluble in mineral acids.

5. **Potassium ferrocyanide** produces a brown precipitate of potassium uranyl ferrocyanide.

$$K_4Fe(CN)_6 + UO_2(NO_3)_2 = [Fe(CN)_6]\begin{matrix} /\!\!/ UO_2 \\ - K \\ \diagdown K \end{matrix} + 2KNO_3$$

In very dilute solutions merely a brown coloration is produced. The brown colour or precipitate can be distinguished from copper ferrocyanide by addition of potassium hydroxide which forms yellow potassium uranate, whilst copper ferrocyanide undergoes no change. Potassium ferrocyanide is employed as an external indicator in the volumetric determination of phosphoric acid with uranyl salts.

Separation of the Metals of the Iron Group.

Several methods of procedure may be adopted for separating the metals of the iron group. The method most generally applicable will be found on p. 217, but in presence of large quantities of **manganese** or **cobalt** or both, the following method will be found more satisfactory. In this case advantage is taken of the insolubility of the sulphides of nickel and cobalt in dilute 2N. hydrochloric acid. The method of procedure, in the absence of phosphoric acid,† is as follows :—

The solution from the **copper group** is evaporated to small bulk, then about one quarter of its volume of ammonium chloride is added to the hot solution, and a slight excess of ammonium hydroxide. This precipitates the **hydroxides of iron, chromium, aluminium,** and **cerium.** Hydrogen sulphide is now added or passed through the unfiltered mixture. This

† If a phosphate is present, the phosphoric acid must first be removed (see p. 118).

precipitates the **sulphides of zinc, manganese, cobalt,** and **nickel,** the iron at the same time being converted into **ferrous sulphide.**

The mixed hydrates and sulphides are filtered off and washed with hot water; then they are transferred to a small flask or test-tube, and mixed with excess of cold dilute hydrochloric acid of the above-mentioned strength. The flask is closed with a cork, and shaken vigorously for two or three minutes. By this treatment the hydrates of **chromium, aluminium,** and **cerium,** together with the sulphides of **iron, manganese,** and **zinc,** are dissolved. The sulphides of **cobalt** and **nickel** are filtered off, and dissolved in 4N. hydrochloric acid with a crystal of potassium chlorate. From this solution cobalt and nickel are separated as described on p. 106.

To the cold solution, which should be transferred to an evaporating dish, **sodium peroxide** is added in small quantities at a time, until the solution is strongly alkaline, when it is boiled until effervescence ceases.† **Sodium aluminate, zincate,** and **chromate** are produced, and go into solution. The iron and cerium are precipitated as **ferric** and **ceric hydroxides,** and the manganese as hydrated **manganese dioxide.** For the further separation of these metals, see table on p. 217.

Separation of Phosphoric Acid from Mixtures.—Seeing that all phosphates are soluble in mineral acids, the presence of the phosphoric acid anion does not interfere with the course of testing for the cations of the silver and copper groups, because the solution is kept acid until these are removed as insoluble chlorides and sulphides. As soon, however, as the solution is rendered alkaline by **ammonium hydroxide,** the insoluble phosphates of the **iron group,** of the **barium group,** and of **magnesium** are precipitated; *e.g.*—

$$FeCl_3 + H_3PO_4 + 3NH_4OH = FePO_4 + 3NH_4Cl + 3H_2O$$

$$CaCl_2 + H_3PO_4 + 2NH_4OH = CaHPO_4 + 2NH_4Cl + 2H_2O \ddagger$$

† Instead of sodium peroxide, sodium hydroxide may be added until the liquid is strongly alkaline, and then hydrogen peroxide; after which, it is treated as already described.

‡ With excess of ammonium hydroxide tricalcium phosphate is produced, $Ca_3(PO_4)_2$.

The metals thus precipitated *need not* have been originally present as phosphates; the presence in the solution of phosphoric acid, liberated by hydrochloric acid and sulphuretted hydrogen from phosphates belonging to the cations of the silver and copper groups, or soluble alkali phosphates, would at this stage cause precipitation of the insoluble phosphate; thus—

$$(NH_4)_2HPO_4 + CaCl_2 = CaHPO_4 + 2NH_4Cl$$

It is apparent, then, that, unless the phosphoric acid be removed before the addition of **ammonium hydroxide,** very serious complications may ensue. Therefore, after having got rid of the metals of the **silver, copper,** and **arsenic groups,** *phosphates should always be tested for.*

Test for Phosphoric Acid.—A small portion of the solution is strongly acidified with concentrated **nitric acid,** a large excess of **ammonium molybdate** is added, and the mixture gently warmed (not boiled); if a canary-yellow precipitate is formed, this shows the **presence of a phosphate.** It may be necessary and is always advisable to allow the mixture to stand for a few minutes.

Removal of the Phosphoric Acid.—The presence of a phosphate having been ascertained, the rest of the solution is neutralised with **ammonium hydroxide** until a slight turbidity is produced. About 2-3 c.c. of a strong solution of **ammonium acetate** are now added, and then ferric chloride, drop by drop, till the solution acquires a permanent red coloration.† On first adding the ferric chloride a yellowish-white precipitate is formed: this is the ferric phosphate precipitate. The appearance of the red coloration shows when the phosphate has been entirely precipitated and ferric acetate (see p. 95) is being formed. As soon as the red colour is permanent, no

† The ammonium acetate is added in order to neutralise the hydrochloric acid set free when ferric chloride reacts with a phosphate, because ferric phosphate is soluble in hydrochloric acid.

(*a*) $Na_2HPO_4 + FeCl_3 \rightleftharpoons FePO_4 + HCl + 2NaCl$

(*b*) $Na_2HPO_4 + FeCl_3 + CH_3.COONH_4 = FePO_4 + NH_4Cl + 2NaCl + CH_3COOH$

more ferric chloride should be added, because ferric phosphate is slightly soluble in this reagent.†

The mixture is now boiled, when the excess of iron is precipitated as basic ferric acetate. The precipitate is filtered off, and the **solution** analysed as usual for the metals of the **iron, barium,** and **sodium** groups by adding ammonium chloride, etc.‡

If, on adding ammonia to a portion of the solution from the copper group, no precipitate is produced, then, even if a phosphate is present, it is not necessary to remove it, because only the alkali metals can be present.

Analysis of Residue.—It sometimes happens that chromium and aluminium are precipitated together with the phosphate; therefore it is always advisable to examine this precipitate for these metals.

Having washed the precipitate, suspend it in water in an evaporating basin, and add sodium peroxide to the cold mixture until strongly alkaline. Now boil until effervescence ceases, and filter off the **ferric hydroxide,** which may be discarded.

The Solution.—Cool and divide into two portions. Acidify the one with acetic acid, and test for chromium by addition of lead acetate: a yellow precipitate shows the presence of **chromium.**

Acidify the second portion with **hydrochloric acid,** add excess of ammonium hydroxide, and boil: a white gelatinous precipitate indicates **aluminium.**

† It sometimes happens that the mixture itself contains sufficient iron to precipitate all the phosphate on the addition of ammonium acetate. In such cases it of course is not necessary to add ferric chloride. Whether or not it is necessary is at once seen on adding the first drop which, if all the phosphate has been precipitated, will colour the solution red owing to formation of **ferric acetate.**

‡ When a phosphate is present it is necessary to examine separately the solution obtained from the **copper group** for iron as follows: A small portion of the solution is boiled with a few drops of concentrated nitric acid to convert the iron into the **ferric** state. **Ammonium thiocyanate** is then added, which, if iron is present, produces a blood-red coloration.

CHAPTER VII.

THE BARIUM GROUP.

THE metals of this group, *viz.* **barium, strontium,** and **calcium,** are often called the metals of the alkaline earths. They all form sparingly-soluble **carbonates** and **sulphates.** Of the sulphates, that of barium is the most insoluble, while that of calcium is the most soluble. Their sulphides are soluble in water, and are therefore not precipitated with the metals of the iron group. Their hydroxides are soluble, and have a strong alkaline reaction. Barium hydroxide is the most soluble, calcium hydroxide the least soluble of the three.

Barium.

Dry Reaction.—Compounds of barium colour the flame of the Bunsen burner a pea-green, which, when viewed through the spectroscope, shows a number of brilliant green bands at α and β. There are also several less intense bands in the green, yellow, and red. Barium chloride is insoluble in **absolute alcohol.**

Reactions in Solution.—Use a solution of **barium chloride.**

*1. **Ammonium carbonate** forms a heavy, white amorphous precipitate of **barium carbonate** which is soluble in dilute acids.

$$BaCl_2 + (NH_4)_2CO_3 = BaCO_3 + 2NH_4Cl$$

*2. **Sulphuric acid** or a soluble **sulphate** produces immediately a white precipitate of **barium sulphate,** insoluble in dilute acids.

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl$$

It is slightly soluble in concentrated hot hydrochloric acid and in concentrated hot sulphuric acid, owing to the formation of an acid sulphate. Dilution with water reprecipitates the barium sulphate.

$$BaSO_4 + H_2SO_4 = Ba(HSO_4)_2$$

It is also easily soluble in sodium thiosulphate.

3. Calcium sulphate, which is only slightly soluble in water, gives a precipitate of barium sulphate. Even strontium sulphate, which is still less soluble, is capable of precipitating barium sulphate from solution.

***4. Potassium chromate** or **dichromate** gives a light yellow precipitate of **barium chromate,** *insoluble* in acetic acid, but soluble in hydrochloric and nitric acids.

$$Ba(NO_3)_2 + K_2CrO_4 = BaCrO_4 + 2KNO_3$$

The precipitation is not complete when potassium dichromate is used, because barium chromate is partially dissolved again by the acid set free in the reaction.

$$2BaCl_2 + K_2Cr_2O_7 + H_2O \rightleftharpoons 2BaCrO_4 + 2HCl + 2KCl$$

It can, however, be made quantitative by adding sufficient of an alkali acetate to replace the free mineral acid by acetic acid.

$$CH_3 . COONa + HCl \rightleftharpoons CH_3 . COOH + NaCl$$

5. Drop Reaction.—Drops of the solution to be tested and of a 5 per cent. solution of sodium rhodizonate produce a brown spot when mixed, if barium or strontium is present. Calcium has no effect, and if strontium is present and the spot is touched with a drop of acid then a red colour indicates barium (sensitiveness 0·5 γ).

Strontium.

Dry Reaction.—Compounds of strontium impart a brilliant crimson coloration to the flame of the Bunsen burner, which,

when seen through the spectroscope, shows several characteristic lines in the orange, blue, and red, which distinguish the spectrum of strontium from that of barium or calcium.

Absolute alcohol dissolves strontium chloride.

Reactions in Solution.—Use a solution of **strontium chloride** or **nitrate.**

*****1. Ammonium carbonate** produces a heavy white precipitate of **strontium carbonate.**

$$Sr(NO_3)_2 + (NH_4)_2CO_3 = SrCO_3 + 2NH_4NO_3$$

*****2. Sulphuric acid** or a **soluble sulphate** gives a white precipitate of **strontium sulphate.** In very dilute solutions the precipitation is slow. Addition of **ammonium sulphate** solution, in which the precipitate is insoluble, causes complete precipitation.

$$SrCl_2 + H_2SO_4 = SrSO_4 + 2HCl$$

Calcium sulphate solution slowly produces a precipitate of strontium sulphate.

3. Potassium chromate forms a light yellow precipitate of **strontium chromate,** which is very readily *soluble* in acetic acid. This precipitate is not produced in dilute solutions. (*Cf.* Barium.)

$$Sr(NO_3)_2 + K_2CrO_4 \rightleftharpoons SrCrO_4 + 2KNO_3$$

4. Ammonium oxalate produces a white precipitate of **strontium oxalate,** practically insoluble in acetic acid.

$$SrCl_2 + \begin{array}{l} COONH_4 \\ | \\ COONH_4 \end{array} = \begin{array}{l} COO \\ | \\ COO \end{array}\!\!>\!Sr + 2NH_4Cl$$

5. Drop Reaction.—The sodium rhodizonate reaction described for barium (§ 5, p. 122) is applied on a filter paper which has first been impregnated with potassium chromate in order to remove any barium as barium chromate (sensitiveness 4 γ).

6. Crystal Test.—A 15 per cent. solution of potassium chromate gives characteristic bunches of prismatic crystals of strontium chromate (sensitiveness 1 γ); barium and much calcium interfere.

Calcium.

Dry Reactions.—Compounds of calcium colour the flame a dull red; the colour, however, is not so intense as that produced by strontium. When viewed through the spectroscope, a bright bluish-green line, β, and a sharp line, α, in the orange are seen; there are also several lines between these. Both the chloride and nitrate are soluble in **absolute alcohol**, and they are also soluble in a mixture of equal volumes of alcohol and ether.

Reactions in Solution.—Use a solution of **calcium chloride.**

***1. Ammonium carbonate** forms a dense white precipitate of **calcium carbonate,** soluble in dilute acids. Precipitation is not complete if a large excess of an ammonium salt is present.

$$CaCl_2 + (NH_4)_2CO_3 \rightleftharpoons CaCO_3 + 2NH_4Cl$$

2. Sulphuric acid produces from strong solutions an immediate precipitate of **calcium sulphate.** In dilute solutions either no precipitation takes place, or only after standing for some time.

***3. Ammonium oxalate** produces a heavy, white powdery precipitate of calcium oxalate, which is insoluble in acetic acid, but soluble in hydrochloric acid.

$$CaCl_2 + \begin{array}{l} COONH_4 \\ | \\ COONH_4 \end{array} = \begin{array}{l} COO \\ | \\ COO \end{array} \!\!\!> Ca + 2NH_4Cl$$

4. Crystal Test.—(*a*) Warm dilute sulphuric acid is added to the solution of calcium containing hydrochloric acid when radiating bunches of fine needles of calcium sulphate (Fig. 17, p. 139) are produced (sensitiveness 0·05 γ), even in the presence of barium and strontium.

(*b*) To a drop of a saturated solution of picrolonic acid on a warm slide is added a drop of the calcium chloride solution, when characteristic rectangular crystals are produced (sensitiveness 0·03 γ). Strontium forms similar crystals, but barium forms needles.

Separation of Barium, Strontium, and Calcium.

There are various ways of separating the metals of the **barium group.** Two methods are here given, the one being based on the different solubilities of the **nitrates** in strong nitric acid, the other on the solubility of calcium nitrate in absolute alcohol.

I. **Ammonium carbonate** is added to the hot solution obtained from the **iron group.** Carbonates of barium, strontium, and calcium are precipitated. They are filtered off, dissolved in dilute nitric acid, and the solution is evaporated nearly to dryness. The pasty mass is taken up with a little concentrated nitric acid, and filtered **cold.** The residue on the filter paper,† which consists of the **nitrates of barium** and **strontium,** is washed with a little strong **nitric acid.** The solution contains the soluble **calcium nitrate.** The barium and strontium nitrates are dissolved in water, and separated by precipitating the barium as **chromate.** For complete table of separation, see p. 221.

NOTE.—After the ammonium carbonate has been added, the mixture should not be boiled, because, as there is excess of ammonium chloride in the solution from the previous group, the calcium carbonate will be partially decomposed, owing to the reaction being reversible.

$$CaCO_3 + 2NH_4Cl \rightleftharpoons (NH_4)_2CO_3 + CaCl_2$$

On the other hand, it is better to have the solution hot before adding the ammonium carbonate, because the solution of ammonium carbonate in the laboratory generally contains **bicarbonate,** which gives rise to the soluble bicarbonates of

† Instead of filter paper it is better to use a wad of asbestos.

the metals of this group. Warming decomposes these bicarbonates into normal carbonates, water, and carbon dioxide.

$$SrCl_2 + 2NH_4HCO_3 \rightarrow \underset{\text{On warming}}{Sr(HCO_3)_2} + 2NH_4Cl \rightarrow SrCO_3 + H_2O + CO_2 + 2NH_4Cl$$

II. To the hot ammoniacal solution of the three metals, add a slight excess of ammonium carbonate and allow to stand for ten minutes. Filter off the carbonates and wash with a little water. Now dissolve the carbonates on the filter paper with the least possible quantity of warm acetic acid. Add excess of K_2CrO_4 to the solution, when a yellow precipitate of **barium chromate** is produced. Filter off, and make the solution just alkaline with ammonium hydroxide and add ammonium carbonate, allow to stand a few minutes and filter. Dissolve the carbonates in a little dilute nitric acid. Evaporate to dryness on the **water bath.** Treat the residue with a little **absolute alcohol,** stir for a minute or two, and filter. Wash the residue on the filter paper with a little alcohol. The residue is **strontium nitrate,** the solution contains **calcium nitrate.** The complete table of separations will be found on p. 221.

It is interesting to note that the salts of the metals of this group which are deliquescent are soluble in absolute alcohol; those which are not are insoluble.

CHAPTER VIII.

THE SODIUM GROUP.

THIS group includes, besides the metals **potassium, sodium, lithium,** and **magnesium,** the compound cation **ammonium** $NH^{\cdot}_4$. The hydroxides of the first three metals are very largely dissociated in solution into the ions $R^{\cdot}$ and OH'; they are, therefore, extremely strong bases. They are not precipitated by ordinary reagents, because they form soluble salts; for this reason, the metals of the group remain in solution at the end of the group separation. Magnesium does not really belong to the alkali metal group (it should, strictly speaking, be classed with the alkaline earths), but, for convenience in analysis, it is placed in this group.

Ammonia, when dissolved in water, exists partly as NH_4OH, which is only slightly ionised; it is a much weaker base than **potassium, sodium,** or **lithium hydroxide.**

Potassium.

The majority of potassium salts are readily soluble in water, and many of them have a strong alkaline reaction, owing to hydrolysis, as, for example, cyanide, borate, and silicate.

Dry Reaction.—*Flame Test.*—Potassium compounds impart a violet coloration to the Bunsen flame. The presence of sodium masks the colour reaction, but on looking at the flame through a piece of blue glass or an indigo prism, the yellow rays emitted by the sodium are cut off, and only those due to the potassium, appearing now as a violet-red, are discernible.

When viewed through the spectroscope, a characteristic red line and an indigo-blue line are seen.

Reactions in Solution.—Use a solution of **potassium chloride** or **nitrate**.

*1. **Hydrogen platinichloride** gives, from neutral or hydrochloric acid solutions, a golden-yellow crystalline precipitate of **potassium platinichloride,** insoluble in alcohol, but soluble in potassium hydroxide.

$$2KCl + H_2PtCl_6 = K_2PtCl_6 + 2HCl$$

This test serves as a **Drop Reaction** (see also Platinum, p. 77). If the solution is very dilute, the precipitation will be hastened by adding a little alcohol and scratching with a glass rod.

*2. **Sodium hydrogen tartrate** or **tartaric acid** produces, in solutions which are not too dilute, a white crystalline precipitate of **potassium hydrogen tartrate.**

$$KCl + \begin{array}{l} CH(OH)COONa \\ | \\ CH(OH)COOH \end{array} = \begin{array}{l} CH(OH)COOK \\ | \\ CH(OH)COOH \end{array} + NaCl$$

The precipitation is accelerated by rubbing the sides of the tube with a glass rod, and by the addition of alcohol. If any mineral acid is present, addition of sodium acetate facilitates precipitation.

*3. **Sodium cobaltinitrite** gives, from solutions which have been strongly acidified with acetic acid, a brilliant yellow precipitate of **potassium cobaltinitrite.** The reaction may be carried out as follows: Add to the solution to be tested about 2 c.c. of a 5 per cent. solution of **cobalt nitrate,** and about an equal volume of a fairly strong solution of **sodium nitrite,** then excess of glacial acetic acid, and about one-third of its volume of alcohol. Either at once, or on shaking, a bright yellow precipitate is produced. The reaction is more readily carried out, and is more delicate, by dissolving about 0·3 grm. of the solid sodium cobaltinitrite (p. 368) in about 2 c.c. of water, and adding the solution to be tested, and about an equal volume of alcohol.

$$3KNO_3 + Na_3Co(NO_2)_6 = K_3Co(NO_2)_6 + 3NaNO_3$$

4. Hydrofluosilicic acid produces a white gelatinous precipitate of potassium silicofluoride.

$$H_2SiF_6 + 2KCl = K_2SiF_6 + 2HCl$$

5. Sodium thiosulphate and bismuth (Carnot's reaction).—Add a drop or two of a dilute solution of bismuth nitrate to 1 to 2 c.c. of a solution of sodium thiosulphate, and then about four times the volume of absolute alcohol (if the solution is not clear a few drops of water may be added). On now adding a few drops of potassium salt a yellow precipitate of **potassium bismuth thiosulphate** is produced.

$$(1) \quad Bi(NO_3)_3 + 3Na_2S_2O_3 = Na_3Bi(S_2O_3)_3 + 3NaNO_3$$
$$(2) \quad Na_3Bi(S_2O_3)_3 + 3KNO_3 = K_3[Bi(S_2O_3)_3] + 3NaNO_3$$

In presence of ammonium chloride this reaction does not take place.

6. Crystal Test.—The triple nitrite reagent (p. 371) gives sharply-defined dark silhouetted squares and rectangles (Fig. 18, p. 139) in the presence of potassium, ammonium, rubidium, cæsium, or thallium (sensitiveness 0·2 γ). Sodium or the alkaline earths do not interfere. This is a very striking reaction, and is very useful as a confirmatory test in the sodium group separation, in conjunction with the sodium test (see § 3, p. 131).

Cæsium and Rubidium.

These metals are nearly always found together and both are very similar in properties to potassium. Separations of the three are based on differences in solubilities of their salts.

1. Antimony trichloride precipitates cæsium chloroantimonite from alkaline solution; potassium and rubidium do not react.

2. Drop Reaction.—A saturated solution of potassium platinic chloride produces small yellow octahedra of cæsium chloroplatinate, which are easily distinguishable from the

larger octahedra of the similar rubidium salt. (See Platinum, § 6, p. 78).

3. Crystal Test.—See Potassium § 6.

Sodium.

Dry Reaction.—*Flame Reaction.*—Sodium compounds, even in extremely minute quantities, colour the flame of the Bunsen burner a brilliant golden-yellow. On viewing the flame through an indigo prism or a piece of blue glass, it appears colourless. When seen through the spectroscope, a single yellow line is visible.

Reactions in Solution.—Use a solution of **sodium chloride.** Owing to the fact that all sodium salts are soluble in water, it is usual to prove the presence of sodium by the flame reaction, having first shown that all other elements are absent.

1. Hydrogen platinichloride gives no precipitate with sodium salts even on addition of alcohol, because the **sodium platinichloride** is soluble both in alcohol and water. On carefully evaporating almost to dryness, however, small triclinic prisms are obtained, whereas those of potassium platinichloride are octahedra. By means of a low power microscope the two salts can readily be distinguished when they are obtained together.

***2. Potassium antimonate** gives from neutral solutions a white crystalline precipitate of **sodium antimonate.** Precipitation is facilitated by shaking and rubbing the sides of the test-tube.

$$KH_2SbO_4 + NaCl = NaH_2SbO_4 + KCl$$

It is decomposed by acids, with formation of **metantimonic acid,** $HSbO_3$

$$NaH_2SbO_4 + HCl = HSbO_3 + NaCl + H_2O$$

Potassium antimonate was formerly thought to be potassium pyroantimonate ($K_2H_2Sb_2O_7, H_2O$). Probably when

the salt is freshly prepared, it is really potassium metantimonate. The fact that when freshly precipitated, the sodium salt is of a rather gelatinous character, and only gradually becomes granular, points to the precipitation of sodium metantimonate which gradually passes into the granular antimonate.

$$\text{(i)} \quad KSbO_3 + NaCl = NaSbO_3 + KCl$$
$$\text{(ii)} \quad NaSbO_3 + H_2O = NaH_2SbO_4$$

3. Crystal Test.—To a cold clear drop of a saturated solution of 4 grms. of uranyl acetate and 4 drops of glacial acetic acid in 100 c.c. of water is added a little of the sodium compound, when well-defined tetrahedra of sodium uranyl acetate $NaC_2H_3O_2, UO_2(C_2H_3O_2)_2$ (Fig. 19, p. 139) are produced in the course of a minute (sensitiveness 0·1 γ). Large quantities of acid interfere, but potassium has no effect unless present in excess. This reaction is very striking, and may be used in conjunction with the reaction described in § 6, p. 129, to distinguish sodium from potassium in the group tests (p. 222).

Ammonium.

Nearly all the ammonium salts are soluble in water.

Dry Reaction.—Many ammonium compounds are volatile when heated, condensing again unchanged on the cool portions of the tube. Some compounds, such as the phosphate, lose ammonia when they are heated; the presence of the ammonia is readily detected by the smell, or by holding the tube near a bottle of strong hydrochloric, when white fumes of ammonium chloride appear (see below).

$$(NH_4)_2HPO_4 = 2NH_3 + \underset{\text{Metaphosphoric acid}}{HPO_3} + H_2O$$

Reactions in Solution.—Use a solution of **ammonium chloride.**

***1. Hydrogen platinichloride** gives a golden-yellow crystalline precipitate of **ammonium platinichloride.**

$$2NH_4Cl + H_2PtCl_6 = (NH_4)_2PtCl_6 + 2HCl$$

On igniting this salt it is decomposed, **ammonium chloride** being volatilised, and a grey residue of platinum remaining behind. When the similar compound of potassium is ignited, a residue of platinum mixed with **potassium chloride** is obtained.

This may be used as a **Crystal Test** if the ammonia is generated by warming the material with alkali in a small dish and the fumes are caught on a drop of 10 per cent. platinum chloride held on the underside of a microscope slide which covers the dish (sensitiveness 0·1 γ).

***2.** All ammonium compounds when boiled with a solution of caustic alkali evolve ammonia which may be recognised by its smell, and by colouring red litmus paper blue, or turmeric paper brown. It also turns a piece of filter paper soaked in a solution of mercurous nitrate black, and produces fumes with hydrochloric acid (see above).

$$NH_4NO_3 + KOH = NH_3 + KNO_3 + H_2O$$

3. Nessler's reagent (p. 370) gives a brown precipitate; even with very dilute solutions a yellowish-brown coloration is produced. The precipitate or coloration is due to formation of **oxydimercuric ammonium iodide.** This test is very delicate and is employed in water analysis.

$$NH_4OH + 2K_2HgI_4 + 3KOH$$
$$= IHg - OHg - NH_2 + 7KI + 3H_2O$$

The precipitate is soluble in the presence of an excess of ammonium salts.

***4. Sodium cobaltinitrite** gives a yellow precipitate of **ammonium cobaltinitrite** $(NH_4)_3Co(NO_2)_6$. (*Cf.* § 3, p. 128.)

5. Drop Reactions.—(*a*) The $NH_4^{\cdot}$ ion gives an intense blue coloration with phenol and a drop of fresh 2N. sodium hypobromite. This turns red on acidification. If a 25 per cent. solution of thymol in alcohol is used in place of phenol, a violet colour is extracted on shaking with ether. Other cations do not interfere.

(*b*) To a drop of the neutral or alkaline solution are added 3 drops of 10 per cent. potassium iodide and a drop of saturated sodium hypochlorite solution. Black nitrogen iodide is precipitated.

$$2NH_4Cl + 2KI + 2NaClO = NHI_2 + NH_3 + 2KCl + 2H_2O + 2NaCl$$

Lithium.

Most lithium compounds are soluble in water. Lithium chloride is soluble in amyl alcohol and in a mixture of alcohol and ether.

Dry Reactions.—*Flame Reaction.*—Compounds of lithium colour the flame of the Bunsen burner a carmine red. On viewing through a thick piece of blue glass or an indigo prism, the flame appears colourless. Seen through the spectroscope, a bright crimson red line and a more feeble orange line are visible.

Reactions in Solution.—Use a solution of **lithium chloride.**

*1. **Sodium phosphate** gives on warming a white crystalline precipitate of **lithium phosphate.** The precipitation is more complete if the solution is first made strongly alkaline with **sodium hydroxide.**

$$3LiCl + Na_2HPO_4 = Li_3PO_4 + 2NaCl + HCl$$

In presence of ammonium salts no precipitate is formed.

*2. **Alkali carbonates** produce from concentrated solutions a white precipitate of **lithium carbonate.**

$$2LiCl + Na_2CO_3 = Li_2CO_3 + 2NaCl$$

Magnesium.

Metallic magnesium is very readily soluble in dilute mineral acids. When exposed to the air it gradually becomes coated with a thin film of oxide. The metal is only slightly soluble

in caustic alkalis, but dissolves readily in solutions of ammonium salts with evolution of hydrogen.

$$Mg + (NH_4)_2SO_4 = MgSO_4 + 2NH_3 + H_2$$

Dry Reactions.—*Blowpipe Test.*—Heated on charcoal before the blowpipe compounds of magnesium become incandescent.

Filter Ash Test.—If a piece of filter paper is moistened with a salt of magnesium and a drop or two of cobalt nitrate, then dried and ignited, the ash assumes a pink tinge.

Reactions in Solution.—Use a solution of **magnesium sulphate.**

1. Sodium or **potassium carbonate** gives a white precipitate of basic **magnesium carbonate.**

$$4MgCl_2 + 4Na_2CO_3 + H_2O$$
$$= 3MgCO_3, Mg(OH)_2 + CO_2 + 8NaCl$$

The precipitation is more complete on boiling. No precipitate is formed in presence of **ammonium salts.**

$$3MgCO_3, Mg(OH)_2 + 8NH_4Cl$$
$$= 4MgCl_2 + 3(NH_4)_2CO_3 + 2NH_3 + 2H_2O$$

2. Ammonium carbonate produces no immediate precipitation, but after some time separation of crystalline **ammonium magnesium carbonate** takes place. In presence of **ammonium salts** this separation does not take place.

$$MgSO_4 + 2(NH_4)_2CO_3 = Mg(NH_4)_2(CO_3)_2 + (NH_4)_2SO_4$$

***3. Ammonium hydroxide** forms a white gelatinous precipitate of **magnesium hydroxide.** The well-washed precipitate is slightly soluble in pure water, and turns red litmus blue. Presence of ammonium salts prevent precipitation, hence the use of ammonium chloride before adding ammonium hydroxide in precipitation of metals of the iron group.

$$MgSO_4 + 2NH_4OH = Mg(OH)_2 + (NH_4)_2SO_4$$

*4. **Sodium phosphate** produces a white amorphous precipitate of **magnesium hydrogen phosphate.**

$$MgCl_2 + Na_2HPO_4 = MgHPO_4 + 2NaCl$$

In presence of **ammonium chloride** and **hydroxide** (the ammonium chloride being added to prevent precipitation of **magnesium hydroxide** by the ammonium hydroxide) a crystalline precipitate of **magnesium ammonium phosphate** is produced.

$$MgSO_4 + Na_2HPO_4 + NH_4OH = Mg(NH_4)PO_4 + Na_2SO_4 + H_2O$$

This precipitate is almost insoluble in water containing **ammonium hydroxide.** From very dilute solutions the precipitate only comes down slowly; its precipitation is facilitated by scratching the sides of the test-tube with a glass rod.

This reaction may also be used as a **Crystal Test** (sensitiveness 0·07 γ).

The explanation of the prevention of precipitation by ammonium salts is as follows (see p. 22): The magnesium hydroxide is slightly soluble in water and is partially ionised into $Mg^{\cdot\cdot}$ and $2OH'$ ions On addition of ammonium chloride, which is strongly ionised into $NH_4^{\cdot}$ and Cl' ions, the OH' ions are taken up by the $NH_4^{\cdot}$ ions to produce unionised or very feebly ionised NH_4OH (or $NH_3 + H_2O$). Hydroxyl ions therefore disappear, and equilibrium is destroyed. Therefore more $Mg(OH)_2$ goes into solution in order to supply more OH' ions, which in turn are taken up by the $NH_4^{\cdot}$, and if sufficient ammonium salt is present this will go on until the whole of the magnesium hydroxide has gone into solution. Addition of an excess of hydroxyl ions by adding a highly ionised base such as KOH, causes a reprecipitation of magnesium hydroxide. In analysis the ammonium salt is added first, because, as already stated, ammonium hydroxide is very slightly ionised in solution, but still sufficiently to cause partial precipitation (see § 3, p. 134). It is, however, very

much less ionised in the presence of its salts. Therefore, if an ammonium salt is first added, the concentration of the hydroxyl ions of the now *very* feebly ionised ammonium hydroxide is not sufficient to cause precipitation of magnesium hydroxide.

5. **Drop Reaction.**—A drop of the solution is acidified with dilute hydrochloric acid, and 1 drop of a 0·5 per cent. solution of *p*-nitrobenzene azo-resorcinol ("magneson") in 0·25 *N* sodium hydroxide is added, followed by 1 drop of 10 per cent. sodium hydroxide; 1 γ of magnesium gives a deep blue colour or precipitate.

Separation of the Metals Potassium, Sodium, and Magnesium.

In testing qualitatively for these metals, it is not usual to separate **magnesium** from potassium and sodium, but to divide the solution obtained from the previous groups into two portions.

To the first and smaller portion a solution of **sodium phosphate** or of **microcosmic salt** and excess of ammonium hydroxide are added, the mixture is thoroughly agitated, and the sides of the test-tube are scratched with a glass rod. The **magnesium** is precipitated as crystalline **magnesium ammonium phosphate,** $Mg(NH_4)PO_4$. Confirm by the "Magneson" reaction.

(*a*) The second and larger portion is evaporated to dryness, and ignited strongly, until no more fumes of **ammonium salts** are given off. It is then cooled and dissolved in a small quantity of water, and acidified with two or three drops of **hydrochloric acid.** To the acid solution excess of hydrogen platinichloride is added, and it is evaporated on a water bath nearly to dryness. A few drops of this solution may be tested for potassium, by Carnot's reaction (§ 5, p. 129). Alcohol is now added (about 5-6 c.c.); this dissolves the **sodium platinichloride,** also that of lithium, should this metal be present.

The potassium salt is insoluble in alcohol, and may be filtered off and washed with a little alcohol. The potassium may be recognised by means of the flame test or spectroscope. The solution is evaporated to dryness, and the residue tested for sodium by means of the flame test or examined under the microscope. Fuller methods of separation will be found on p. 222.

NOTE.—It is a matter of the utmost importance that the whole of the ammonium salts should be volatilised, because **ammonium salts** also give an insoluble **platinichloride.** It is not unusual for students to imagine that they have discovered potassium in the substance they are examining, whereas the supposed potassium platinichloride is ammonium platinichloride, and is simply a result of careless working. Again, students, through careless manipulation, often do not find potassium when it really is present. This is traceable to imperfect washing of precipitates and non-reservation of the washings, and also to the fact that, on evaporating to dryness prior to the elimination of the ammonium salts, the evaporation is conducted in such a manner that most of the salts are lost by spirting out of the dish. This is easily prevented if, as soon as the concentration of the solution has become so great that further heating on the sand bath causes spirting, the evaporating basin is placed on a water bath until quite dry. It may then be ignited without danger of loss by spirting. Let the student bear in mind that a little extra time spent over an operation in order to ensure accuracy is not **lost.** Much more time is **lost** by having to go through the whole analysis again.

(*b*) Sodium is also quantitatively precipitated in the presence of potassium on addition of an equal volume of a 5 per cent. solution of dihydroxy tartaric acid which has previously been neutralised with potassium hydroxide to phenolphthalein. It is advisable to stir well and to allow the mixture to stand overnight, preferably in some ice-water. After filtration, the liquid may be used for the potassium cobaltinitrite test (§ 3, p. 128).

(*c*) The uranyl acetate reaction (§ 3, p. 131) may also be used for the removal of sodium from potassium as

$$NaZn(UO_2)_3 (C_2H_3O_2)_9, 6H_2O$$

if the mixture contains less than 80 per cent. of the latter.

If it is desired to remove the **magnesium,** this may be done by evaporating the whole of the solution from the **barium group** to dryness, and igniting to get rid of the ammonium salts. The residue is then dissolved in water, and **barium hydroxide** solution added until an alkaline reaction is obtained. The mixture is then boiled, and the **magnesium hydroxide** is filtered off. The excess of barium hydroxide is removed by adding ammonium hydroxide and carbonate, boiling and filtering. The solution is examined for **potassium** and **sodium** as above after evaporating and igniting to remove the ammonium salts.

Test for the Ammonium Radical.

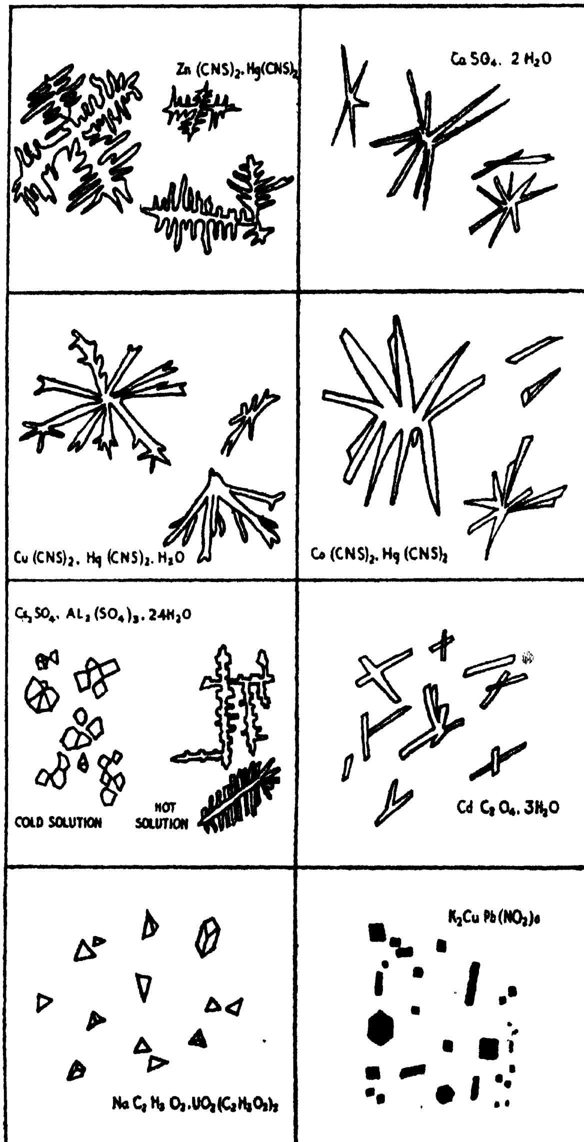
As, during the course of analysis, ammonium salts have been repeatedly added, ammonium cannot be tested for at this stage; but a small portion of the original substance is boiled with caustic soda, the ammonia is liberated, and can be recognised by the tests given above (p. 131).

FIG. 15. FIG. 17.

FIG. 9. FIG. 16.

FIG. 14. FIG. 10.

FIG. 19. FIG. 18.



Crystal Tests.

CHAPTER IX.

THE ACIDS.

THE acids are electrolytes which contain the cation $H^{\cdot}$, which is replaceable by metals with formation of **salts.** Acids are strong or weak according to whether they are ionised to a great or small extent respectively, at a given concentration. The **strong acids** are **sulphuric** and **nitric acids,** the **halogen acids** (with the exception of hydrofluoric acid), **chloric acid** and a few others. Among those which are only ionised to a moderate extent, and are therefore only moderately strong, are **phosphoric, sulphurous,** etc., and many of the **organic acids** such as **formic** and **acetic** acids. The acids which are only very slightly ionised include **hydrogen sulphide solution, hydrocyanic, carbonic, silicic** and **boric acids.** These are **weak acids,** and are incapable of forming neutral salts with the strong bases, their salts with the strong bases all having an alkaline reaction owing to hydrolysis. Acids which are weak or only moderately strong have a much feebler acidic effect in the presence of **neutral salts** containing the same anion. Thus, *e.g.* **acetic acid,** which is classed with the moderately strong acids, is a very weak acid in presence of **sodium acetate,** because the ionisation of the acetic acid is lowered, and fewer $H^{\cdot}$ ions are produced (see p. 16).

Grouping of the Acids.

To arrange a separation for the acid radicals (anions) which will be as thorough and reliable as the methods employed in separating the metallic or basic radicals (cations) is not practicable. Nevertheless, it is possible to place the anions into

groups, according to their behaviour with such reagents as **silver nitrate** and **barium chloride,** and by this means a rough separation can be made. According to this arrangement the acids fall into five groups.

Group I.—Silver nitrate produces a white precipitate, insoluble in nitric acid.

Barium chloride produces no precipitate.

This group includes—HCl, HBr, HI (light yellow),† HCN, $H_4Fe(CN)_6$, $H_3Fe(CN)_6$ (orange-yellow), HClO, HCNS.

Group II.—Silver nitrate produces a precipitate, soluble in nitric acid.

Barium chloride produces no precipitate.

This group includes—HNO_2, H_2S (black), H_3PO_2, H_2SO_3, $H_2S_2O_8$ (black).

Group III.—Silver nitrate produces a precipitate, soluble in nitric acid.

Barium chloride produces a white precipitate, soluble in nitric acid.

This group includes—H_3PO_4 (yellow), HPO_3, H_3PO_3, $H_4P_2O_7$, $H_2S_2O_3$ (brown), H_3BO_3, H_3AsO_3 (yellow), H_3AsO_4 (chocolate), H_2CrO_4 (red), H_2SiO_3 (orange), HIO_3 (difficultly soluble in HNO_3), H_2CO_3.

Group IV.—Barium chloride produces a white precipitate, insoluble in acids.

Silver nitrate produces no precipitate.

This group includes—H_2SO_4, HF.

Group V.—Barium chloride produces no precipitate.

Silver nitrate produces no precipitate.

This group includes—HNO_3, $HClO_3$, $HClO_4$, $HMnO_4$.

NOTE.—It must be remembered that silver nitrate gives a brown precipitate of silver oxide from alkaline solutions of hydroxides.

† Colours refer to the precipitates with silver nitrate, which are white unless otherwise stated.

As far as possible the acids in the succeeding pages have been arranged according to the above grouping. But in certain cases—for studying the reactions of the acids—it is more convenient to vary this arrangement slightly. Thus, for example, in the grouping of the acids, sulphuric acid occurs in Group IV., and sulphurous acid in Group II. But for studying the reactions, sulphuric and sulphurous acids have been placed together.

Hydrochloric Acid.

HCl

All chlorides, except silver, mercurous, and lead chlorides, are soluble in water. Chlorides of bismuth, tin, and antimony are soluble only in water containing free hydrochloric acid.

1. Most chlorides, when warmed with concentrated sulphuric acid, give off fumes of hydrochloric acid.

$$(a)\quad 2KCl + H_2SO_4 = K_2SO_4 + 2HCl$$
$$(b)\quad MnCl_2 + H_2SO_4 = MnSO_4 + 2HCl$$

***2. Silver nitrate** forms a white curdy precipitate of **silver chloride.**

$$NaCl + AgNO_3 = AgCl + NaNO_3$$

When exposed to light it gradually turns violet, and, finally, black. It is insoluble in nitric acid, but readily soluble in ammonium hydroxide, potassium cyanide, or in sodium thiosulphate (*cf.* Silver, p. 35). This test makes an excellent **Drop Reaction.**

***3. Lead acetate** gives a white crystalline precipitate of **lead chloride,** soluble in boiling water, from which it crystallises again on cooling in small needles.

$$2KCl + (CH_3COO)_2Pb = PbCl_2 + 2CH_3COOK$$

4. On mixing a chloride with **manganese dioxide,** adding concentrated **sulphuric acid,** and gently warming, chlorine gas is liberated, which may be recognised by its yellow colour, by

its smell, and by bleaching a strip of moist litmus paper held in the mouth of the tube.

$$2NaCl + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$$

*5. When a dry chloride is mixed with an excess of potassium dichromate and a few cubic centimetres of concentrated sulphuric acid, and then distilled from a small distilling flask, **chromyl chloride** is formed, which condenses in the receiver as a heavy brownish-red fuming liquid.

$$4NaCl + K_2Cr_2O_7 + 3H_2SO_4 = 2CrO_2Cl_2 + 2Na_2SO_4 + K_2SO_4 + 3H_2O$$

The chromyl chloride dissolves in water, forming a yellow solution of chromic acid, which, on addition of ammonium or sodium hydroxide, is converted into ammonium or sodium chromate.

$$CrO_2Cl_2 + 4NH_4OH = 2NH_4Cl + (NH_4)_2CrO_4 + 2H_2O$$

On now acidifying with acetic acid, and adding **lead acetate**, a yellow precipitate of **lead chromate** is produced. Bromide, if it were present, would form a compound soluble in the ammonium hydroxide, forming a colourless solution, and on the addition of lead acetate no yellow precipitate would be produced. If, however, the bromine was there in considerable quantity, a white precipitate of $PbBr_2$ might be produced, soluble in boiling water.

Hydrobromic Acid.

HBr

Bromides, with the exception of those of silver, mercury, lead, bismuth, antimony, and tin, are soluble in water.

*1. **Silver nitrate** gives a very pale yellow precipitate of **silver bromide**, which is insoluble in nitric acid, and soluble, with difficulty, in ammonia; it is, however, readily soluble in potassium cyanide.

$$NaBr + AgNO_3 = AgBr + NaNO_3$$

2. Lead acetate precipitates white crystalline lead bromide, almost insoluble in cold water, but fairly soluble on boiling.

$$2KBr + (CH_3COO)_2Pb = PbBr_2 + 2CH_3COOK$$

***3.** Concentrated **sulphuric acid** liberates a portion of the bromine from a bromide, while a portion becomes hydrobromic acid.

$$(a)\quad 2KBr + H_2SO_4 = 2HBr + K_2SO_4$$
$$(b)\quad 2HBr + H_2SO_4 = 2H_2O + SO_2 + Br_2$$

***4.** When a mixture of a bromide and **manganese dioxide** is heated with concentrated **sulphuric acid,** free bromine is obtained, recognised by its heavy brown vapour and unpleasant odour. In this case the whole of the bromine is liberated.

$$2KBr + MnO_2 + 2H_2SO_4 = Br_2 + K_2SO_4 + MnSO_4 + 2H_2O$$

***5. Chlorine water,** when added drop by drop to a solution of a bromide, liberates bromine, which colours the liquid brown.

$$2KBr + Cl_2 = 2KCl + Br_2$$

On shaking the solution with chloroform or carbon disulphide, the bromine dissolves, forming a coloured layer. On addition of a further quantity of chlorine water, the brown colour gradually disappears, owing to the formation of colourless bromic acid.

$$Br_2 + 5Cl_2 + 6H_2O = 2HBrO_3 + 10HCl$$

6. Drop Reaction.—The solution is boiled in a small test-tube with lead dioxide and dilute acetic acid, and the bromine vapours evolved are caught on a filter paper impregnated with a solution of fluorescein in 50 per cent. alcohol. The red tetra-bromofluorescein is produced by 2 γ of bromine, and is unaffected by chlorides, although iodides interfere.

7. Crystal Tests.—Silver bromide is precipitated in the usual way and dissolved in ammonia. (*a*) On evaporation characteristic rectangles are deposited. (*b*) Platinum sul-

phate deposits octahedra of ammonium platinum bromide in the presence of sulphuric acid, and addition of a crystal of potassium bisulphate produces octahedra of potassium platinum bromide (sensitiveness 0·5 mgrm.).

Hydriodic Acid.

HI

Nearly all the iodides are soluble in water, but many of them only with difficulty. With the exception of silver iodide, they are all soluble in acids.

*1. **Silver nitrate** gives a heavy, curdy light yellow precipitate of **silver iodide.**

$$KI + AgNO_3 = AgI + KNO_3$$

It is insoluble in nitric acid and in ammonium hydroxide, but soluble in potassium cyanide and in sodium thiosulphate.

2. **Lead acetate** produces a yellow crystalline precipitate of **lead iodide,** soluble in boiling water, from which it recrystallises in shiny glistening leaflets.

$$2KI + (CH_3COO)_2Pb = PbI_2 + 2CH_3COOK$$

*3. **Mercuric chloride** forms a yellow precipitate of **mercuric iodide,** which immediately changes to deep red. (*Cf.* Mercury, p. 39.) The precipitate is soluble in excess of mercuric chloride, and also in excess of potassium iodide.

$$2KI + HgCl_2 = HgI_2 + 2KCl$$

4. Concentrated **sulphuric acid** decomposes iodides, a portion being liberated as free iodine.

$$(a)\quad 2KI + H_2SO_4 = K_2SO_4 + 2HI$$
$$(b)\quad 2HI + H_2SO_4 = I_2 + SO_2 + 2H_2O$$

The reaction appears to take place partly in the following manner, the sulphuric acid being still further reduced.

$$8HI + H_2SO_4 = H_2S + 4H_2O + 4I_2$$

5. Concentrated **sulphuric acid** and **manganese dioxide** liberate iodine.

$$2KI + MnO_2 + 2H_2SO_4 = MnSO_4 + I_2 + K_2SO_4 + 2H_2O$$

The iodine may be distilled, when it passes over as violet vapours, crystallising on the cool portions of the receiver in small, dark, shining crystals.

***6.** **Chlorine water,** or a solution of **bleaching powder,** when added drop by drop to a solution of an iodide, liberates iodine. The presence of the liberated iodine can be shown, even if the quantity is extremely small, by adding a few drops of starch paste, when the deep blue coloration of **iodide of starch** is produced.

Iodine is more soluble in chloroform and carbon disulphide than in water. If 2 c.c. of either of these solvents are added to the solution containing free iodine, and the mixture is shaken up, the solvent dissolves the iodine, forming a violet layer at the bottom of the test-tube. The appearance of this colour provides a very sensitive test for iodine. Excess of chlorine water causes the coloration to disappear, owing to the **iodine** being converted into iodic acid.

$$I_2 + 6H_2O + 5Cl_2 = 2HIO_3 + 10HCl$$

***7.** A very delicate test for iodine may be carried out as follows: Acidify the solution with dilute sulphuric acid, and add a few drops of starch paste, then a small scrap of zinc, and 1 drop of nitric acid. Iodine will be liberated and cause a deep blue coloration of the starch. When sulphuric acid is added to an iodide, hydriodic acid is produced, which by itself does not colour starch. But on addition of zinc and nitric acid, the hydrogen evolved by the action of the zinc on the sulphuric acid reduces the nitric acid to nitrous acid (p. 165),

and this, acting on the hydriodic acid, liberates iodine, which with the starch forms blue "iodide of starch."

$$HNO_3 + H_2 = HNO_2 + H_2O$$

This may be used as a **Drop Reaction.**

Detection of Chloride, Bromide, and Iodide in Mixtures.—Since these three substances form insoluble silver salts, they are all precipitated on adding silver nitrate to a solution which has been acidified with nitric acid.

(*a*) Silver iodide may be separated from silver chloride and bromide, owing to its insolubility in ammonia; whereas the others readily dissolve in warm ammonium hydroxide.

(*b*) A bromide and iodide may readily be detected when they occur together by carefully adding **chlorine water** to the dilute neutral solution, and shaking up with about 2 c.c. of **carbon disulphide** or **chloroform.** The chlorine first liberates the iodine, which dissolves in the lower layer of chloroform or carbon disulphide, forming a violet solution. The upper aqueous solution may now be decanted or removed with a pipette into another test-tube, containing a little chloroform, and chlorine again added. If the whole of the iodine has already been liberated, the further addition of chlorine water will now liberate bromine, and the chloroform will become brown. In the event of the iodine not having been entirely liberated in the first instance, the chloroform will become coloured violet, but on adding more chlorine water the violet colour will gradually fade away (§ 6, p. 146), and the brown due to the bromine will take its place. Further addition of chlorine water will finally cause the brown colour of the bromine to vanish.

Instead of using chlorine water, add to the neutral solution a solution of **bleaching powder** †: this liberates the iodine from the iodide, but has no action on the bromide. Extract

† Only a very small quantity of bleaching powder should be added in the first place, because, if there is very little iodine, the excess of bleaching powder almost immediately oxidises it to iodic acid.

the iodine from the solution with chloroform or carbon disulphide; add a little more bleaching powder, and, if a further quantity of iodine is liberated, again extract. As soon as all the iodine has been removed, pour off the colourless aqueous solution, and add a drop of acetic acid. The acid liberates chlorine from the calcium hypochlorite, which then reacts with the bromide, liberating bromine. On now shaking with chloroform, the bromine dissolves in this solvent with formation of a brown solution at the bottom of the aqueous layer. If no bromine is present, the liquid will be coloured yellow, owing to liberation of chlorine, but, when shaken up with chloroform or carbon disulphide, both the lower layer and the upper aqueous layer take on nearly the same yellow tint; whereas, when bromine is present, the lower layer becomes a more or less intense brown, the upper one being either light yellow or colourless.

(*c*) It is, of course, necessary to test a separate portion of the mixture for chloride. This is best done by taking a little of the solid substance and distilling it with **potassium dichromate** and concentrated **sulphuric acid**, when chromyl chloride will distil over. (Cf. § 5, p. 143.) The distillate may be made alkaline with ammonia, acidified with dilute sulphuric acid, and tested for a chromate with **hydrogen peroxide**, or acidified with acetic acid and **lead acetate** added.

(*d*) **Separation of Iodine as Cuprous Iodide.**—Saturate the solution with **sulphur dioxide**, or add 2 or 3 c.c. of a strong solution of **sulphurous acid**. Now add excess of copper sulphate, when the iodine will be precipitated as **cuprous iodide**. After filtering, boil the solution till free from **sulphurous acid**, and divide into two portions. Test one portion for bromine, by the addition of **chlorine water** in presence of carbon disulphide. Evaporate the second portion to dryness, and apply the **chromyl chloride test**.

As a matter of fact, cuprous iodide is actually precipitated by the addition of copper sulphate to a solution of potassium iodide, thus—

$$2CuSO_4 + 4KI = Cu_2I_2 + 2K_2SO_4 + I_2$$

Probably, in the first place, cupric iodide is formed, which is almost immediately converted into cuprous iodide with liberation of iodine.†

$$2Cu^{\cdot\cdot} + 4I' \rightleftharpoons Cu_2I_2 + I_2$$

The reaction, however, is never complete, a certain quantity of copper always remaining in solution, a balanced condition being produced, as shown in the equation. The addition of SO_2 removes one of the reaction products—the liberated iodine. The equilibrium balance thus being destroyed, the reaction is enabled to complete itself. (See p. 22.)

Detection of Chloride, Bromide, and Iodide in Presence of Cyanides.—Cyanides give a white curdy precipitate with **silver nitrate**, which is almost identical in appearance, solubility, and general chemical reactions with silver chloride. If, in the preliminary tests, the presence of a cyanide has been discovered, it is better to remove it before testing for the halogens. This may be done (i) by boiling the solution with dilute **nitric acid** ; (ii) by passing **carbonic acid gas** through the solution, and then boiling; or (iii) by boiling with excess of **sodium bicarbonate.** The operation *must* be conducted in a draught cupboard, as the gas is poisonous.

If it has been precipitated with the halogens, it may be removed by (*a*) boiling with strong nitric acid, (*b*) fusing the mixed silver salts, when silver cyanide will be decomposed, cyanogen being evolved and silver remaining.

Hypochlorous Acid.

HClO

This acid is only known in aqueous solution, and in the form of its salts. When a solution of an alkali hypochlorite

† The reduction may be supposed to take place by the cupric ions losing one of their + charges, the charge becoming neutralised with the — charge of an iodine ion.

is boiled it is converted into a mixture of a chloride and a chlorate; *e.g.*—

$$3NaClO = 2NaCl + NaClO_3$$

*1. On treating a hypochlorite with dilute **sulphuric** or **hydrochloric acid,** chlorine gas is evolved.

$$NaClO + 2HCl = Cl_2 + H_2O + NaCl$$
$$4NaClO + 2H_2SO_4 = 2Cl_2 + 2Na_2SO_4 + 2H_2O + O_2$$

2. **Silver nitrate,** when added to a solution of a hypochlorite which has been neutralised with dilute nitric acid, gives a white precipitate of silver chloride. The silver hypochlorite which is first produced is converted into silver chloride and chlorate. This change is more rapid and complete on boiling.

$$(a)\quad NaClO + AgNO_3 = AgClO + NaNO_3$$
$$(b)\quad 3AgClO = 2AgCl + AgClO_3$$

*3. **Lead acetate** produces a white crystalline precipitate of **lead chloride,** which, in the cold, gradually becomes orange-yellow, and finally brown, owing to its conversion into **lead peroxide.** These changes take place rapidly on boiling.

*4. When shaken up with **mercury,** hypochlorous acid or a slightly acidified solution of a hypochlorite covers the surface of the mercury with a yellow or brown scum of **oxide of mercury** or **mercuric oxychloride.** The scum or precipitate, when separated from the mercury, dissolves in warm dilute hydrochloric acid, the solution giving the reactions for mercury.

$$2HClO + 2Hg = HgO, HgCl_2 + H_2O$$

This reaction serves to distinguish **hypochlorous acid** *from* **chlorine.** A solution of chlorine when shaken up with mercury forms an insoluble precipitate of white **mercurous chloride,** which is also insoluble in warm dilute hydrochloric acid. If, therefore, the precipitate formed by shaking hypochlorous acid and chlorine with mercury is warmed with dilute hydrochloric acid, the brownish part of it will dissolve, leaving unchanged the white **mercurous chloride:** the presence of

hypochlorous acid is confirmed by finding mercury in the acid solution.

Hydrocyanic Acid (Prussic Acid).

HCN

Hydrocyanic acid is an exceedingly weak acid, being very *feebly* ionised in solution ; therefore, owing to hydrolysis, the alkali metal salts have a strongly alkaline reaction. The salts and solutions of the alkali cyanides possess a strong smell of hydrocyanic acid, because in solution they are hydrolysed thus—

$$(K^{\cdot} + CN') + (H^{\cdot} + OH') = (K^{\cdot} + OH') + \underset{\text{(not ionised)}}{HCN}$$

The hydrocyanic acid not being to any extent ionised is there as such, hence the smell—this also explains the alkalinity, because as the $H^{\cdot}$ ions are taken up by the CN' to form un-ionised HCN, hydroxyl ions become free. The solution, therefore, contains un-ionised HCN and $K^{\cdot}$ and OH' ions.

The cyanides of the alkali metals and alkaline earths are soluble in water ; the cyanides of the other metals are insoluble, but are decomposed by dilute acids with evolution of hydrocyanic acid. Most of the insoluble cyanides dissolve in a solution of **potassium cyanide,** forming soluble salts, *e.g.* $KAg(CN)_2$, from which the silver cannot be precipitated by ordinary reagents, because it is in the **anion** $Ag(CN)_2'$.

Dry Reactions.—The alkali cyanides are not decomposed on heating, but silver or mercury cyanide yields cyanogen, which can be recognised by its burning with a pink flame, and by its unpleasant smell. (Caution, the gas is very poisonous.)

$$Hg(CN)_2 = (CN)_2 + Hg$$

Ferrous cyanide, on ignition, gives iron carbide and nitrogen.

$$2Fe(CN)_2 = 2FeC_2 + N_2$$

Wet Reactions.—Use a solution of potassium cyanide.

*1. **Hydrochloric acid** decomposes most soluble cyanides in the cold with evolution of hydrocyanic acid, but those of the heavy metals are only decomposed on heating.

$$KCN + HCl = HCN + KCl$$

Hydrocyanic acid is extremely poisonous, and the greatest care must be taken when working with it.

*2. **Silver nitrate** produces a white, curdy precipitate of **silver cyanide.**

$$KCN + AgNO_3 = AgCN + KNO_3$$

On adding small quantities of silver nitrate to a solution of potassium cyanide, the precipitate dissolves as soon as it is formed, owing to the solubility of silver cyanide in potassium cyanide. The precipitation, therefore, is only complete when the silver nitrate is added in excess.

$$AgCN + KCN = KAg(CN)_2$$

Silver cyanide is also readily soluble in ammonium hydroxide. It is decomposed on ignition with evolution of cyanogen, a residue of silver remaining. When boiled with concentrated nitric acid it also decomposes (distinction from silver chloride).

*3. Add a few drops of yellow ammonium sulphide to a few drops of a solution of a cyanide, and evaporate to dryness on the water bath; then moisten the residue with dilute hydrochloric acid and a few drops of water, and again evaporate, nearly to dryness. On now adding ferric chloride, a blood-red coloration will be produced, owing to the formation of **ferric thiocyanate. Ammonium thiocyanate** is, in the first place, produced by the action of the ammonium sulphide on the cyanide.

$$(1)\quad NH_4CN + (NH_4)_2S_2 = NH_4CNS + (NH_4)_2S$$

$$(2)\quad 3NH_4CNS + FeCl_3 = Fe(CNS)_3 + 3NH_4Cl$$

*4. When a mixture of a cyanide with caustic alkali and ferrous sulphate, to which a few drops of ferric chloride have

been added, is boiled, and then acidified with hydrochloric acid, a deep blue precipitate of "Prussian blue" is obtained. If the quantity of cyanide is very small a blue coloration only is produced.

$$(1)\quad Fe(OH)_2 + 6KCN = K_4Fe(CN)_6 + 2KOH$$

$$(2)\quad 4FeCl_3 + 3K_4Fe(CN)_6 = Fe_4[Fe(CN)_6]_3 + 12KCl$$

*5. To a mixture of a cyanide with 10 to 15 drops of a mixture of **sodium nitrate** and **ferric chloride** solutions dilute sulphuric acid is added until a yellow coloration is produced. The mixture is gently warmed, then cooled, and the excess of ferric salt is removed by the addition of ammonium hydroxide and filtration. On adding a drop of ammonium sulphide to the filtrate, a violet coloration is produced. The reaction is due to the formation of **sodium nitroprusside.** (*Cf.* § 3, p. 170.)

Hydroferrocyanic Acid.

$$H_4Fe(CN)_6$$

The ferrocyanides of the alkali metals are soluble in water, those of the alkaline earths difficultly soluble; most of the other ferrocyanides are insoluble in water and dilute acids.

1. When a ferrocyanide is heated with concentrated **sulphuric acid, carbon monoxide** is evolved.

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O$$
$$= 6CO + 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4$$

2. On heating with dilute **sulphuric acid, hydrocyanic acid** is produced.

$$2K_4Fe(CN)_6 + 3H_2SO_4$$
$$= K_2Fe[Fe(CN)_6] + 3K_2SO_4 + 6HCN$$

3. Silver nitrate produces from freshly prepared solutions a white precipitate of **silver ferrocyanide,** which is insoluble in ammonium hydroxide, but soluble in potassium cyanide.

$$K_4Fe(CN)_6 + 4AgNO_3 = Ag_4Fe(CN)_6 + 4KNO_3$$

From solutions which have been prepared for some time the precipitate may be flesh-coloured.

4. Ferrous salts precipitate white **potassium ferrous ferrocyanide,** which rapidly turns blue, owing to oxidation.

$$K_4Fe(CN)_6 + FeSO_4 = K_2Fe[Fe(CN)_6] + K_2SO_4$$

The precipitate is usually light blue, even when freshly precipitated, owing to oxidation of the ferrous sulphate.

***5. Ferric chloride** produces an intense blue precipitate of **ferric ferrocyanide,** " Prussian blue " (**Drop Reaction**).

$$3K_4Fe(CN)_6 + 4FeCl_3 = Fe_4[Fe(CN)_6]_3 + 12KCl$$

It is insoluble in dilute acids, but soluble in oxalic acid, with formation of a deep blue solution. Potassium or sodium hydroxide decomposes Prussian blue, **ferric hydroxide** and **potassium ferrocyanide** being formed.

$$Fe_4[Fe(CN)_6]_3 + 12KOH = 3K_4Fe(CN)_6 + 4Fe(OH)_3$$

It is interesting to notice that only the iron which is present in the **cation** is precipitated as ferric hydroxide on the addition of caustic alkali. That which occurs in the compound anion is unaffected.

***6. Copper sulphate** gives a purplish-brown precipitate of **cupric ferrocyanide.** In very dilute solutions a purplish-brown coloration and no precipitate is produced. The precipitate is insoluble in acetic acid.

$$K_4Fe(CN)_6 + 2CuSO_4 = Cu_2Fe(CN)_6 + 2K_2SO_4$$

Hydroferricyanic Acid.

$$H_3Fe(CN)_6$$

The ferricyanides of the alkali and alkaline earth metals are soluble in water: those of the other metals are insoluble, both in water and in dilute acids.

1. Concentrated and dilute **sulphuric acid** behave with ferricyanides in the same manner as with ferrocyanides.

2. Silver nitrate produces a reddish-brown precipitate of **silver ferricyanide,** which has the appearance of ferric hydroxide. It is only partially soluble in ammonium hydroxide, a white residue being left behind.

$$K_3Fe(CN)_6 + 3AgNO_3 = Ag_3Fe(CN)_6 + 3KNO_3$$

***3. Ferrous sulphate** produces an intense blue precipitate of **ferrous ferricyanide, "Turnbull's blue."** It is insoluble in oxalic acid (**Drop Reaction**).

$$2K_3Fe(CN)_6 + 3FeSO_4 = Fe_3[Fe(CN)_6]_2 + 3K_2SO_4$$

Sodium hydroxide decomposes "Turnbull's blue" with formation of sodium ferricyanide and ferrous hydroxide, only the iron which is present in the **cation** being converted into ferrous hydroxide.

$$Fe_3[Fe(CN)_6]_2 + 6NaOH = 2Na_3Fe(CN)_6 + 3Fe(OH)_2$$

4. Ferric chloride forms no precipitate, but the colour changes to olive-brown. (See § 4, p. 94.)

The iron contained in the ferro- and ferricyanides cannot be precipitated by the usual reagents, because it is in the anion. In solution we have the ions $4K^{\cdot}$ and $Fe(CN)_6''''$ and $3K^{\cdot}$ and $Fe(CN)_6'''$, respectively, the potassium, of course, being the cation. In ferrocyanides the anion is tetravalent, but in the ferricyanides it is trivalent.

Thiocyanic Acid (Sulphocyanic Acid).

HCNS

The thiocyanates, with the exception of those of lead, silver, mercury, and copper, are soluble in water.

***1. Silver nitrate** gives a white curdy precipitate of **silver thiocyanate,** soluble in a large excess of ammonia.

$$KCNS + AgNO_3 = AgCNS + KNO_3$$

***2.** On adding **copper sulphate** to a thiocyanate, no precipitate is produced, but the colour becomes greenish. If

the thiocyanate is in excess, a black precipitate is gradually formed. On adding a mixture of **copper sulphate** and **sulphurous acid**, a white or grey precipitate of **cuprous thiocyanate** is produced, owing to the reduction of the cupric thiocyanate first produced.

$$2KCNS + 2CuSO_4 + SO_2 + 2H_2O = Cu_2(CNS)_2 + K_2SO_4 + 2H_2SO_4$$

***3. Ferric chloride** produces an intense blood-red coloration of **ferric thiocyanate** (**Drop Reaction**).

$$3KCNS + FeCl_3 = Fe(CNS)_3 + 3KCl$$

The coloration is destroyed by addition of **mercuric chloride** or of **rochelle salt.** It is soluble in ether. (*Cf.* § 5, p. 95.)

4. Mercuric nitrate gives a white precipitate of **mercuric thiocyanate.**

$$2KCNS + Hg(NO_3)_2 = Hg(CNS)_2 + 2KNO_3$$

Detection of Ferrocyanides, Ferricyanides, and Thiocyanates in a Mixture.—To the solution, which has been acidified with hydrochloric acid, add **ferric chloride** in excess. A deep blue precipitate of "Prussian blue" shows the presence of a **ferrocyanide.** Filter off this precipitate. If the solution has a blood-red colour, this shows that a **thiocyanate** is present. The red colour may, however, be masked by the brown colour produced by the action of the excess of ferric chloride on the ferricyanide. It is therefore better to shake up with a little ether: the red ferric thiocyanate will colour the ethereal layer red.

Now, in order to test for the **ferricyanide,** add a few drops of hydrogen peroxide or stannous chloride, either of which will reducc the excess of ferric chloride to ferrous chloride, which will then react with any ferricyanide which may be present, and give a blue precipitate of Turnbull's blue.

When cyanides are present with ferro- and ferricyanides, and it is desired to get rid of, or to test the mixture for cyanide

before testing for the above double cyanides, the mixture should be distilled with **sodium** or **potassium bicarbonate,** which only decomposes the cyanide, the double cyanides being unattacked. The distillate must be tested for the cyanide, the residue being tested for the double cyanides.

In all cases in which hydrocyanic acid is evolved, great caution must be used, owing to the extremely poisonous nature of the substance, and *all operations must be conducted in the draught cupboard.*

Insoluble Double Cyanides.—Before testing, insoluble ferrocyanides must be converted into soluble salts. The substance is boiled with caustic soda, and, after diluting, the solution is filtered from any insoluble residue. The insoluble double cyanides are, by this treatment, converted into sodium ferro- or ferricyanides and a hydroxide of the metal; *e.g.*—

$$Cu_2Fe(CN)_6 + 4NaOH = Na_4Fe(CN)_6 + 2Cu(OH)_2$$

The filtrate, after acidifying with dilute hydrochloric acid, is tested as already described.

Treatment of a Mixture containing Cyanogen Compounds before proceeding to analyse for the Bases (Cations).—The presence of ferro- or ferricyanides will have been indicated when examining the substance in the dry way; (1) by the odour of cyanogen produced when the mixture was heated in a dry tube; (2) on treating the substance with hydrochloric acid, when a blue or green solution is obtained, or, if insoluble, by the blue or green coloration of the residue. Before proceeding to the separation of the metals, it is necessary that cyanogen compounds should be removed. This may be done in several ways.

(i) If the double cyanide is ignited with from three to four times its bulk of a mixture of equal parts of ammonium nitrate and sulphate, the bases unite with SO_4'' to form sulphates, and the cyanide anions are destroyed. The ignition should be performed in a draught cupboard, and should be carried on until all the ammonium salts have been volatilised. The

residue should then be dissolved in water or dilute hydrochloric acid, and examined for bases as usual. If an insoluble residue remains, it will consist of insoluble sulphates, and must be fused with fusion-mixture. The acids must be tested for in a solution prepared as in (ii).

(ii) Boil the mixture with a considerable quantity of a strong solution of caustic alkali; then add a little solid sodium carbonate, and boil again for about five minutes. Dilute with water, and filter. The solution contains all the acids, besides the alkali salts of such metals as aluminium, zinc, lead, etc. The residue contains all the other metals, and should be dissolved in hydrochloric acid and examined for these as usual (p. 211).

Carbonic Acid.

H_2CO_3

This acid is formed when **carbon dioxide** dissolves in water, but owing to its instability, it has not been isolated. The acid is very slightly ionised: this explains its feeble acid reaction, and the fact that its normal salts, which are soluble in water, have an alkaline reaction. This is due to hydrolysis. Potassium carbonate is ionised into $2K^{\cdot}$ and CO_3'', but in the water present there are $H^{\cdot}$ and OH' ions, although only in minute quantities. The tendency is for $H^{\cdot}$ and CO_3'' ions to unite to form unionised H_2CO_3, and this uses up the $H^{\cdot}$ ions, leaving the hydroxyl ions. More water molecules become ionised, with the formation of more unionised H_2CO_3, and the alkalinity of a solution of potassium carbonate is thus due to the presence of OH' ions (as alkalinity is in all cases). The normal carbonates, with the exception of those of the alkali metals, are insoluble in pure water, though many of them are soluble in water containing carbonic acid, owing to formation of **bicarbonates**. They are precipitated from such a solution on boiling.

$$CaCO_3 + H_2O + CO_2 \underset{\text{on boiling}}{\overset{\text{in the cold}}{\rightleftarrows}} Ca(HCO_3)_2$$

1. When strongly heated, all the carbonates, with the exception of barium carbonate and those of the alkali metals, are decomposed with evolution of carbon dioxide, *e.g.*—

$$CuCO_3 = CuO + CO_2$$

***2.** All carbonates, when acted upon by dilute acids, effervesce with evolution of carbon dioxide.

$$BaCO_3 + 2HCl = BaCl_2 + CO_2 + H_2O$$
$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + CO_2 + H_2O$$

If the evolved gas is passed into lime-water, or a solution of barium hydroxide, the liquid becomes turbid owing to precipitation of **calcium** or **barium carbonate,** which is insoluble in water, but soluble in water containing excess of carbonic acid.

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

The best way of applying this test is to place the carbonate in a test-tube, add some acid, and then to bring the end of a glass rod which has been dipped in lime-water into the mouth of the tube. The evolved carbon dioxide causes the lime-water to become turbid. Care must be taken that the glass rod does not come in contact with the mineral acid on the inside of the tube (see also § 5).

***3. Barium chloride** when added to a solution of a carbonate produces a white precipitate of barium carbonate. The precipitate dissolves readily in dilute hydrochloric or nitric acid,—distinction from sulphates.

$$BaCl_2 + Na_2CO_3 = BaCO_3 + 2NaCl$$

***4. Silver nitrate** gives a white precipitate of **silver carbonate** soluble in nitric acid (distinction from chlorides), ammonium hydroxide, or in ammonium carbonate.

$$K_2CO_3 + 2AgNO_3 = Ag_2CO_3 + 2KNO_3$$

5. Drop Reaction.—The liberation of a gas by acid from a drop of solution is conveniently observed under the low power of the microscope. (See Fig. 5, p. 29.)

If a drop of a solution containing 1 c.c. of *N* sodium carbonate, 2 c.c. of 0·5 per cent. phenolphthalein, and 10 c.c. of water is placed on the underside of a microscope slide and held over the warm mixture of carbonate and acid, then the carbon dioxide will remove the red colour owing to the formation of sodium bicarbonate. Nitrous and acetic acids behave similarly; sulphites or sulphides should first be oxidised with a drop of hydrogen peroxide, and cyanides should be precipitated with a drop of saturated mercuric chloride.

Bicarbonates.

Bicarbonates are readily converted into normal carbonates on heating. The **bicarbonates** of the alkali metals are, compared with those of other metals, relatively stable; but they, too, are readily converted into normal carbonates when heated.

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

Some normal carbonates give off carbon dioxide when heated at comparatively low temperatures; but if they have been previously dried at 100°, they will not give off water, as a bicarbonate, however, would. Hence the presence of a bicarbonate in a mixture containing only **alkali metals** may be demonstrated by heating some of the substance in a dry test-tube, the sides of which will become coated with moisture, and testing the gas evolved with lime-water. Further, the normal carbonates of the alkali metals are very much more soluble in water than the acid or bicarbonates, therefore they may be roughly separated by washing. In general, bicarbonates show the same reactions as the normal carbonates, but since they are more acidic, they do not produce the red colour with phenolphthalein. (See § 5 above.)

Bromide Test.—To a solution of bleaching powder add about 1 c.c. of a solution of potassium bromide and 2 c.c. of chloroform or carbon disulphide. On the addition of a solution of a bicarbonate bromine is liberated, which, on shaking,

dissolves in the chloroform, which becomes brown. The reaction is due to liberation of hypochlorous acid by the bicarbonate thus—

$$NaHCO_3 + NaOCl = HClO + Na_2CO_3$$
$$2HClO + 2KBr = Br_2 + 2KCl + H_2O + O$$

Nitric Acid.

HNO_3

Nitric acid when pure is colourless, but it has usually a yellow appearance owing to dissolved oxides of nitrogen. All nitrates, with the exception of basic mercury and bismuth nitrates, are soluble in water.

Dry Reactions.—**1.** All nitrates deflagrate when heated with charcoal.

2. The nitrates of the alkali metals are decomposed, when strongly heated, into a **nitrite** and **oxygen.**

$$2NaNO_3 = 2NaNO_2 + O_2$$

The nitrates of the heavy metals are converted into an oxide or metal with evolution of oxygen and of brown fumes of nitrogen peroxide.

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$
$$(a) \quad 2Hg(NO_3)_2 = 2HgO + 4NO_2 + O_2$$
$$(b) \quad 2HgO = 2Hg + O_2$$

The nitrates of the alkali metals when heated with **copper sulphate** also yield nitrogen peroxide.

$$4NaNO_3 + 2CuSO_4 = 2Na_2SO_4 + 2CuO + 4NO_2 + O_2$$

Wet Reactions.—Use a solution of potassium nitrate.

1. Concentrated **sulphuric acid** when added to a nitrate liberates nitric acid, the vapours of which have a slight brownish-yellow colour.

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$

If, however, a small piece of copper is added to this mixture, deep brown fumes are produced, owing to the formation of nitric oxide by the action of the liberated nitric acid on the copper. The oxygen from the air causes the nitric oxide to be converted into brown nitrogen peroxide.

$$(1)\quad 8HNO_3 + 3Cu = 3Cu(NO_3)_2 + 2NO + 4H_2O$$
$$(2)\quad 2NO + O_2 = 2NO_2 \text{ (brown vapours)}$$

*2. **Brucine.**—To a few drops of a nitrate solution in the bottom of a porcelain basin add 3 to 4 c.c. of concentrated sulphuric acid, and 1 c.c. of a solution of brucine in sulphuric acid. (See Reagents, p. 371.) A rose-red coloration gradually deepening in intensity is produced, which slowly changes to yellow. When carried out as a **Drop Reaction** this test has a sensitiveness of 0·1 γ, but it is not reliable in presence of bromides or iodides. It serves to distinguish *nitrates* in presence of *nitrites* if sodium azide is first added to decompose the latter.

$$N_3Na + HNO_2 = N_2 + N_2O + NaOH$$

*3. When concentrated sulphuric acid is poured cautiously from a pipette down the side of a test-tube containing a cold mixture of concentrated solutions of **ferrous sulphate** and of **nitrate,** a brown ring is obtained, where the heavier sulphuric acid comes in contact with the supernatant liquid. This brown coloration is due to an unstable compound of ferrous sulphate and nitric oxide ($2FeSO_4 . NO$), the formation of which may be thus explained—**sulphuric acid** liberates **nitric acid** from the **nitrate**; **nitric acid** oxidises **ferrous sulphate** to **ferric sulphate,** and is itself reduced to nitric oxide; the **nitric oxide** unites with the still unoxidised portion of the **ferrous sulphate.**

$$2KNO_3 + 4H_2SO_4 + 6FeSO_4$$
$$= K_2SO_4 + 2NO + 3Fe_2(SO_4)_3 + 4H_2O$$

This test is *not* reliable in presence of iodides, bromides, or nitrites.

***4. Reduction.**—A very delicate test, and one which can be carried out in presence of iodides and bromides, depends on the formation of a nitrite by nascent hydrogen. Dissolve in the solution of the nitrate a small crystal of potassium iodide, then add a little starch paste, 2 c.c. of dilute sulphuric acid, and a small piece of zinc. A blue coloration, which first begins to show round the zinc, indicates the presence of a nitrate.

$$(a) \quad HNO_3 + 2H = HNO_2 + H_2O$$
$$(b) \quad 2HNO_2 + 2HI = I_2 + 2NO + 2H_2O$$

If the nitrate is boiled with zinc dust and potassium hydroxide, reduction is more complete, ammonia being evolved.

$$KNO_3 + 4Zn + 7KOH = 4K_2ZnO_2 + 2H_2O + NH_3$$

This reaction is used to distinguish nitrates from chlorates.

5. Crystal Test.—A crystal of " nitron " (Diphenyl-endanilo dihydro-triazole) is added to a solution of the nitrate containing acetic acid, and the mixture is warmed. On cooling bunches of fine needles of nitron nitrate are produced. The test is also given by other anions, including bromides, iodides, nitrites, chromates, oxalates and picrates, although the nitron nitrate is the least soluble and may be used as a means of determining nitrates.

Nitrous Acid.

HNO_2

Nitrous acid is only known in the form of its salts, which are mostly soluble in water.

Dry Reaction.—All nitrites deflagrate when heated with charcoal.

Wet Reaction.—Use a solution of sodium or potassium nitrite.

***1.** Mineral acids and acetic acid decompose nitrites. Nitric oxide is liberated, and this combining with the oxygen

of the air produces brown fumes of nitrogen peroxide; *part of the nitrous acid is converted to nitric acid.*

$$(1)\quad 2KNO_2 + H_2SO_4 = 2HNO_2 + K_2SO_4$$
$$(2)\quad 3HNO_2 = HNO_3 + H_2O + 2NO$$

2. A crystal of **ferrous sulphate** when added to a solution of a nitrite is turned deep brown at once, even in the absence of acid.

3. With sulphuric acid and ferrous sulphate a brown coloration is produced, as with nitrates.

4. Silver nitrate gives from solutions which are not too dilute a white precipitate of **silver nitrite,** soluble in boiling water.

$$AgNO_3 + NaNO_2 = AgNO_2 + NaNO_3$$

5. Meta-phenylenediamine hydrochloride gives a very intense yellow coloration when added to a very dilute solution of a nitrite slightly acidified with acetic acid. This test is extremely delicate, and is used in water analysis. *Nitrates do not give it.* It depends on the formation of **triaminoazobenzene** (Bismarck brown). In strong solutions a brown precipitate is produced.

$$2C_6H_4(NH_2)_2 + HNO_2 = C_6H_4\begin{cases} NH_2 \\ N = N \,.\, C_6H_3(NH_2)_2 \end{cases} + 2H_2O$$

6. On adding a small crystal of **potassium iodide** and some **starch paste** to a solution of a nitrite, and acidifying with a few drops of dilute sulphuric acid, a deep blue coloration is produced (distinction from nitrates). (*Cf.* also § 7, p. 146.)

7. Drop Reactions.—Drops of fresh 0·3 per cent. sulphanilic acid and 0·07 per cent. α-naphthylamine, both in 20 per cent. acetic acid, are added in succession to the nitrite, when a red dye is formed with 0·15 γ of nitrite (this is a form of diazo reaction (see § 2, p. 321), and is known as the Griess reaction).

Tests Nos. 5 and 6 may also be used as drop reactions.

Detection of Nitrates in Presence of Nitrites.—(i) Add to the solution to be tested one or two grams of **urea,** then carefully add dilute sulphuric acid. The nitrous acid is decomposed, and nitrogen and carbon dioxide are evolved.

$$CO(NH_2)_2 + 2HO . NO = 2N_2 + CO_2 + 3H_2O$$

As soon as evolution of gas ceases, a little more urea is added, and the mixture is gently warmed to ensure complete decomposition of the nitrite. Cool the solution, and add a small crystal of potassium iodide and a few drops of starch paste. If the nitrite has been completely destroyed, no coloration will be obtained; but on addition of a small scrap of zinc a blue colour is produced, owing to the nitric acid being reduced to nitrous acid, which then liberates iodine from the potassium iodide. (*Cf.* § 4, p. 163.)

$$HNO_3 + 2H = HNO_2 + H_2O$$

(ii) Instead of using urea, the substance containing the nitrate and nitrite may be boiled for some minutes with **ammonium chloride,** which decomposes the nitrite thus—

$$NaNO_2 + NH_4Cl = NaCl + 2H_2O + N_2$$

It is then tested as already described above.

(iii) By means of the **brucine** test, § 2, p. 162.

Sulphuric Acid.

$$H_2SO_4$$

The neutral sulphates, with the exception of those of **barium, strontium,** and **lead** (slightly soluble), are soluble in water. Many basic sulphates, however, are insoluble.

Dry Reaction.—All sulphates, when heated on charcoal with fusion mixture, are converted into **alkali sulphides.**

$$BaSO_4 + 2C + Na_2CO_3 = Na_2S + BaCO_3 + 2CO_2$$

On dissolving the fused mass in water, filtering and adding a drop of the solution to a drop of **sodium nitroprusside** on a

watch-glass, an intense violet coloration is produced (p. 170); or if a drop of the solution is placed on a silver coin, a black stain is obtained.

Wet Reactions.—Use a solution of sodium or magnesium sulphate.

***1. Barium chloride** gives, with sulphuric acid or soluble sulphates, a heavy white precipitate of **barium sulphate,** which is insoluble in mineral acids (**Drop Reaction**).

$$Na_2SO_4 + BaCl_2 = BaSO_4 + 2NaCl$$

***2. Lead acetate** produces a white precipitate of **lead sulphate,** which is soluble in **ammonium acetate, ammonium tartrate,** or **caustic potash.** Lead sulphate is also slightly soluble in water, but its complete precipitation may be secured by the addition of alcohol.

$$K_2SO_4 + (CH_3COO)_2Pb = PbSO_4 + 2CH_3COOK$$

3. Crystal Test.—The characteristic crystals of calcium sulphate (see § 4, p. 124) may be produced by the action of calcium acetate.

Persulphuric Acid.

$$H_2S_2O_8$$

Persulphuric acid is only known in solution; it is obtained by the electrolysis of strong sulphuric acid. The alkali persulphates, however, are fairly stable.

Dry Reaction.—When persulphates are heated, they are decomposed with evolution of oxygen and sulphuric anhydride.

$$Na_2S_2O_8 = Na_2SO_4 + SO_3 + O$$

Wet Reactions.—Use a solution of ammonium or potassium persulphate.

***1. Potassium iodide** when added to a solution of a persulphate is slowly decomposed in the cold, rapidly on heating, iodine being deposited.

$$K_2S_2O_8 + 2KI = 2K_2SO_4 + I_2$$

*2. **Barium chloride** produces no immediate precipitate, but, on warming, a precipitate of barium sulphate is formed, the barium persulphate at first produced being decomposed.

$$BaS_2O_8 + H_2O = BaSO_4 + H_2SO_4 + O$$

*3. **Silver Nitrate.**—On adding silver nitrate to a solution of a persulphate, a black precipitate of silver peroxide is produced.

$$2AgNO_3 + K_2S_2O_8 + 2H_2O = 2KHSO_4 + 2HNO_3 + Ag_2O_2$$

A concentrated solution of ammonium persulphate and ammonia is treated with a very small quantity of silver nitrate; a vigorous evolution of nitrogen takes place, and the solution becomes very hot. This is probably due to the oxidising action of the silver peroxide formed in the first instance, although it has also been ascribed to *catalysis*.

4. **Drop Reaction.**—In common with many oxidising agents a blue colour is produced with benzidine (sensitiveness 0·5 γ).

Sulphurous Acid.

H_2SO_3

Sulphurous acid is formed when **sulphur dioxide** dissolves in water; but, because of its instability, it has not been isolated. As it is only slightly ionised in aqueous solution, it is not a strong acid, and its normal salts with the alkali metals have an alkaline reaction. Being a dibasic acid, it also forms acid salts or **bisulphites.**

Dry Reaction.—When a **sulphite** is heated on charcoal with fusion mixture, an alkali sulphide is formed. (*Cf.* Sulphates.)

Wet Reactions.—Use a solution of sodium sulphite.

*1. **Sulphuric** or **hydrochloric acid** liberates gaseous **sulphur dioxide,** the presence of which can be detected by its smell (that of burning sulphur), or by catching it on a filter paper

impregnated with potassium iodate, when iodine is liberated and the blue starch iodide is produced. No precipitation of sulphur is produced (distinction from thiosulphates).

$$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + SO_2 + H_2O$$

*2. In solutions which are not too dilute, **barium chloride** gives a white precipitate of **barium sulphite** soluble in hydrochloric acid. (*Cf.* Sulphates, § 1, p. 166.)

$$K_2SO_3 + BaCl_2 = BaSO_3 + 2KCl$$

3. **Silver nitrate** precipitates white **silver sulphite**, soluble in hot dilute nitric acid and in ammonium hydroxide.

$$K_2SO_3 + 2AgNO_3 = Ag_2SO_3 + 2KNO_3$$

Silver sulphite is decomposed on boiling, turning grey owing to deposition of silver and formation of silver sulphate.

$$2Ag_2SO_3 = Ag_2SO_4 + 2Ag + SO_2$$

*4. **Ferric chloride** produces a red coloration, which undergoes no change on standing; but, on boiling, a brown basic iron salt is precipitated (distinction from thiosulphates).

*5. On adding a few drops of a neutral solution of a sulphite to a mixture of dilute solutions of **zinc sulphate** and **sodium nitroprusside**, a red coloration is either at once produced, or immediately becomes visible on adding a small quantity of **potassium ferrocyanide** (distinctive test in presence of thiosulphates).

*6. Owing to the readiness with which sulphurous acid is converted into sulphuric acid by oxidation, it acts as a strong reducing agent. A solution of potassium permanganate is decolorised, and solutions of chromates are turned green owing to their conversion into chromic salts.

(*a*) $$5H_2SO_3 + 2KMnO_4 + 3H_2SO_4 = 5H_2SO_4 + K_2SO_4 + 2MnSO_4 + 3H_2O$$

(*b*) $$3H_2SO_3 + K_2Cr_2O_7 + H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O$$

7. Drop Reaction.—A drop of a weak solution of malachite green held on the underside of a slide is decolorised by 1 γ of sulphur dioxide, even in the presence of thiosulphates.

Detection of Sulphates and Sulphites.—Acidify the solution with hydrochloric acid and add excess of **barium chloride.** From an acid solution only **barium sulphate** will be precipitated; filter this off. The filtrate contains sulphurous acid with excess of barium chloride; add **bromine water,** which will oxidise the sulphurous acid to sulphuric acid, when a further precipitate of barium sulphate will in consequence be produced.

$$H_2SO_3 + Br_2 + H_2O = H_2SO_4 + 2HBr$$

Hydrogen Sulphide (Sulphuretted Hydrogen).

$$H_2S$$

Hydrogen sulphide is only a weak acid, as it is only slightly ionised in solution, and for this reason the normal salts of the alkali metals have a strong alkaline reaction; they are very readily soluble in water. The sulphides of most of the other metals are insoluble in water, but dissolve with decomposition in acids. Aqua regia is the only **acid** which dissolves the sulphides of **mercury, arsenic, platinum,** and **gold.**

Dry Reaction.—When heated on charcoal with fusion mixture, soluble alkali sulphides are formed. (*Cf.* Sulphates, p. 165.)

Wet (and **Drop**) **Reactions.**—Use a solution of ammonium sulphide.

***1. Silver nitrate** when added to a solution containing a sulphide gives a black precipitate of **silver sulphide,** soluble in nitric acid, and in aqua regia.

$$Na_2S + 2AgNO_3 = Ag_2S + 2NaNO_3$$

***2. All sulphides (except those of mercury, silver, arsenic, platinum, and gold), when heated with concentrated hydrochloric acid, give off hydrogen sulphide.** The presence of this

may be shown by the blackening of a piece of filter paper, moistened with lead acetate and held over the test-tube; or by the violet colour imparted by the gas to a piece of paper moistened with sodium nitroprusside and a drop of dilute ammonia.

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$$

*3. **Sodium nitroprusside,** $Na_2Fe(NO)(CN)_5$, when added on a watch-glass, to a drop of a solution of a sulphide, which has been rendered alkaline with sodium hydroxide, produces a violet coloration.

Thiosulphuric Acid.

$$H_2S_2O_3$$

This acid is only known in the form of its salts, which are almost all readily soluble in water. The sodium salt $Na_2S_2O_3$, $5H_2O$ is the " hypo " of the photographer.

Dry Reactions.—**1.** When ignited with fusion mixture on charcoal, a soluble **sulphide** is produced. (*Cf.* Sulphates, p. 165.)

2. When ignited alone decomposition ensues, and part of the sulphur burns.

Wet Reactions.—Use a solution of sodium thiosulphate.

***1.** Dilute mineral acids decompose thiosulphates with liberation of **sulphur dioxide** and precipitation of **yellow sulphur.**

$$Na_2S_2O_3 + 2HCl = SO_2 + S + H_2O + 2NaCl$$

2. Barium chloride gives no precipitate in dilute solutions; but, on addition of a few drops of **bromine water,** a white precipitate of **barium sulphate** is produced.

(*a*) $Na_2S_2O_3 + Br_2 + H_2O = Na_2SO_4 + S + 2HBr$

(*b*) $Na_2SO_4 + BaCl_2 = BaSO_4 + 2NaCl$

3. Silver nitrate, when added in excess, produces a white precipitate of **silver thiosulphate.** When added in small

quantities the precipitate at first formed dissolves in the excess of the thiosulphate.

$$Na_2S_2O_3 + 2AgNO_3 = Ag_2S_2O_3 + 2NaNO_3$$

On boiling, silver thiosulphate turns first yellow, then brown, and finally black.

$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4$$

*4. **Ferric chloride** produces a reddish-violet coloration with alkali thiosulphates. The colour disappears on warming. Even at ordinary temperatures it gradually fades away owing to the violet **ferric thiosulphate**, first formed, being converted into **ferrous thiosulphate** and **ferrous tetrathionate.**

$$(a) \quad 3Na_2S_2O_3 + 2FeCl_3 = Fe_2(S_2O_3)_3 + 6NaCl$$

$$(b) \quad Fe_2(S_2O_3)_3 = FeS_2O_3 + FeS_4O_6$$

Detection of Sulphur Acids in a Mixture.—It is necessary that the **sulphide** be first removed, and this must be done without decomposing the sulphites or thiosulphates, and therefore the solution must not be acidified.

To remove the sulphide shake up with **lead carbonate,** which turns black, being converted into lead sulphide. Filter off the mixture of ~~cadmium~~ Lead carbonate and sulphide. To the filtrate add excess of **strontium nitrate** to precipitate the sulphate and sulphite. Filter off the mixed strontium salts, and treat the precipitate on the filter paper with dilute hydrochloric acid to decompose the sulphite. The strontium sulphate remains on the filter paper, but the sulphite is decomposed, sulphurous acid being produced, which passes through in the filtrate, and may be tested for by adding bromine water, when a white precipitate of strontium sulphate is produced (see p. 123), or by decolorising a solution of iodine.

The **thiosulphate** is tested for in the solution left after filtering off the mixed strontium salts. The solution is acidified with hydrochloric acid and warmed, when the thiosulphate is decomposed, sulphur being precipitated and sulphur dioxide evolved.

Hydrofluoric Acid.

HF

Hydrofluoric acid is a colourless mobile liquid, which fumes strongly in the air. It cannot be kept in glass vessels owing to its corrosive action, but is kept in vulcanite flasks, or platinum bottles. The fluorides of the alkali metals, and of silver, nickel, iron, tin, and mercury, are readily soluble in water, the others being insoluble, or only soluble with great difficulty.

***1.** Fluorides, when heated with concentrated **sulphuric acid** in a lead or platinum vessel, give off vapours of **hydrofluoric acid**; *e.g.*—

$$CaF_2 + H_2SO_4 = 2HF + CaSO_4$$

On holding over the vessel for a short time a clock-glass, which has been covered with a thin coating of wax, and scratched at places with a pin so as to expose the surface of the glass, it is found, on removing it and cleaning off the wax, that the glass has been etched at the exposed portions.

***2.** When a mixture of a fluoride is heated with concentrated sulphuric acid in a test-tube, the hydrofluoric acid which is liberated combines with the silica of the glass to form **silicon tetrafluoride,** which is partially evolved as a gas, but also forms oily globules beneath the surface of the acid. On holding a moistened glass rod in the vapour, the water decomposes the silicon tetrafluoride with formation of silicic acid, which is deposited on the rod as a white film.

$$(a) \quad 4HF + SiO_2 = SiF_4 + 2H_2O$$

$$(b) \quad 3SiF_4 + 3H_2O = H_2SiO_3 + \underset{\text{Hydrofluosilicic acid}}{2H_2SiF_6}$$

Wet Reaction.—Use a solution of sodium fluoride.

***1. Barium chloride** produces a white precipitate of **barium fluoride,** which, on warming with a large excess of mineral acid, dissolves. No precipitate is produced in presence of excess of ammonium salts.

$$2NaF + BaCl_2 = BaF_2 + 2NaCl$$

2. Drop Reaction.—Soluble fluorides or hydrofluoric acid will bleach a mixture of 1 drop of 50 per cent. acetic acid and 1 drop of the coloured solution prepared by mixing excess of an alcoholic solution of alizarin and 0·05 per cent. zirconium oxide in dilute hydrochloric acid. The yellow colour produced with hydrogen peroxide and a titanium salt (p. 191) is also bleached.

Silicic Acid.

H_2SiO_3

Silicic acid is one of the weakest inorganic acids, being scarcely ionised at all in solution. The silicates of the alkali metals are soluble in water, to which they impart a strong alkaline reaction; all other silicates are insoluble. A few of the insoluble silicates are decomposed by acids; *e.g.*—

$$CaSiO_3 + H_2SO_4 = H_2SiO_3 + CaSO_4$$

The majority, however, are not decomposed in this manner. All the silicates of the alkali metals are decomposed, even by dilute acids.

Dry Reactions.—***1.** On fusing a little silica in a microcosmic bead, the silica usually does not dissolve, but floats about in the bead, producing on cooling an opaque bead or a bead enclosing a more or less web-like structure.

2. When a piece of filter paper is moistened with a solution of a soluble silicate and a drop of cobalt nitrate, then dried over the Bunsen flame and ignited, the ash assumes a deep blue tint.

***3.** On mixing silica or a silicate with a powdered fluoride and concentrated sulphuric acid, and heating the mixture as described in § 2, p. 172, for fluorides, **silicon tetrafluoride** is formed, and may be tested for as already described. This test must be made in a platinum or lead dish.

Wet Reactions.—Use a solution of sodium silicate (water-glass).

1. When excess of a dilute mineral acid is added to the solution of a silicate, the silicic acid assumes a colloidal state, but is thrown out in the form of a jelly on concentrating the solution on a water bath.

$$Na_2SiO_3 + 2HCl = H_2SiO_3 + 2NaCl$$

After evaporating to dryness, it is no longer soluble in water.

***2. Silver nitrate** produces an orange-coloured precipitate of **silver silicate,** soluble in acids and in ammonium hydroxide.

$$Na_2SiO_3 + 2AgNO_3 = Ag_2SiO_3 + 2NaNO_3$$

3. Calcium chloride gives a white precipitate of **calcium silicate** which is soluble in acids.

$$Na_2SiO_3 + CaCl_2 = CaSiO_3 + 2NaCl$$

4. Drop Reaction.—A drop of the solution is gently warmed in a porcelain micro-crucible with 1 drop of a solution prepared by pouring 100 c.c. of a 5 per cent. solution of ammonium molybdate into 35 c.c. of 6N. nitric acid. To the cool mixture is added 1 drop of a 5 per cent. solution of benzidine in 10 per cent. acetic acid, and a few drops of a saturated solution of sodium acetate. A blue colour ("molybdenum blue") results from 0·5 γ of SiO_2.

Phosphates and arsenates also give this colour, so the mixture should first be precipitated with ammonium molybdate (see § 3, p. 176); the silica compound only is soluble in nitric acid, and a drop of the filtrate may therefore be used for the above test.

Analysis of Silicates.—In analysing a mixture containing insoluble silicates, it is necessary that they should be decomposed and the bases rendered insoluble.

The substance should be finely powdered, first in an ordinary mortar and finally in an agate mortar. It is then mixed with three or four times its weight of fusion mixture, and fused before the blowpipe until no more carbon dioxide is evolved,

i.e. until effervescence ceases. A soluble silicate is thus obtained; *e.g.*—

$$BaSiO_3 + NaKCO_3 = BaCO_3 + NaKSiO_3$$

On adding dilute hydrochloric acid till an acid reaction is obtained, the bases are converted into chlorides with evolution of carbon dioxide, and **silicic acid** is obtained, which, however, is in the colloidal state.

$$NaKSiO_3 + BaCO_3 + 4HCl = BaCl_2 + H_2SiO_3 + NaCl + KCl + CO_2 + H_2O$$

By evaporating this solution to dryness on the water bath and heating the residue in the oven at about 140° C., the **silicic acid** is converted into **silica** (SiO_2) or a polysilicic acid, *e.g.* $H_2Si_3O_7$, which is insoluble in water. The bases can now be obtained in solution by washing several times with warm dilute hydrochloric acid, the silica remaining as an insoluble residue.

Phosphoric Acid (Orthophosphoric Acid).

$$H_3PO_4$$

The phosphates of the alkali metals are soluble in water; those of the other metals dissolve only in mineral acids.

Dry Reaction.—Phosphates, when burned on a piece of filter paper with cobalt nitrate, impart a blue coloration to the ash; or if the phosphate is heated on charcoal before the blowpipe, moistened with cobalt nitrate, and again heated, a blue mass is obtained.

Wet Reactions.—Use a solution of disodium phosphate Na_2HPO_4.

1. **Calcium chloride** gives a white precipitate of **calcium phosphate,** which is soluble in acetic acid and in mineral acids.

$$Na_2HPO_4 + CaCl_2 = CaHPO_4 + 2NaCl$$

*2. **Silver nitrate** produces a canary-yellow precipitate of **silver phosphate,** soluble in nitric acid and in ammonium hydroxide.

$$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3$$

*3. **Ammonium molybdate,** when added to a solution of a phosphate strongly acidified with concentrated nitric acid, produces at once, or on warming, a canary-yellow powdery precipitate of **ammonium phosphomolybdate.**

$$12[MoO_3](NH_4)_3PO_4.$$

It is soluble in excess of phosphoric acid and in ammonium hydroxide. Arsenates and silicates produce similar precipitates (see § 4, p. 174), that from the latter being soluble in nitric acid.

*4. **Magnesia mixture** (p. 369) gives a white crystalline precipitate of **magnesium ammonium phosphate,** which is insoluble in ammonia, but readily soluble in acids. Arsenates give an analogous reaction. (See § 5, p. 65.)

$$Na_2HPO_4 + MgSO_4 + NH_4OH$$
$$= (NH_4)MgPO_4 + Na_2SO_4 + H_2O$$

*5. **Ferric chloride** produces a yellowish-white precipitate of **ferric phosphate.**

$$Na_2HPO_4 + FeCl_3 \rightleftharpoons FePO_4 + 2NaCl + HCl$$

The precipitate is soluble in excess of ferric chloride and in mineral acids, but is *insoluble* in acetic acid. In order that the above reaction may be quantitative, sodium acetate should be added to replace the free hydrochloric acid liberated in the reaction by acetic acid.

The close relationship between phosphorus and arsenic is strikingly shown in the reactions of **phosphoric** and **arsenic acids,** both of which are tribasic and react with the same reagents.



for example, with a nitric acid solution of molybdic acid and with ammonium magnesium chloride. In a similar manner **phosphorus acid** (H_3PO_3) and **arsenious acid** (H_3AsO_3) may also be compared, although the resemblance is not so striking as in the case of the higher acids.

Silicic acid should first be separated by the molybdate test in the presence of nitric acid which dissolves only ammonium silicomolybdate. (See § 4, p. 174.)

6. Drop Reaction.—A drop each of 5 per cent. ammonium molybdate in 5N. sulphuric acid, 20 per cent. sodium sulphite and 0·5 per cent. hydroquinone in 1 per cent. of N. sulphuric acid are added to 2 drops of the phosphate, when a permanent blue colour gradually develops. The mechanism of the reaction is similar to that used for silicates (see p. 174), but it is insensitive to them unless they are present in large quantities.

Separation of Phosphoric, Silicic and Arsenic Acids.

Both phosphoric and arsenic acid give a yellow precipitate with **ammonium molybdate**, and a white crystalline precipitate with **magnesia mixture**; therefore they must be separated, in order to identify them. Of course, in analysing for the bases, phosphoric acid is always tested for after the arsenic has been precipitated by hydrogen sulphide, and before proceeding to the analysis of the iron group.

Add excess of **magnesia mixture** to the solution, shake up, and allow to stand five to ten minutes. A white crystalline precipitate, consisting of a mixture of $Mg(NH_4)PO_4$ and $Mg(NH_4)AsO_4$, is produced. Filter this off, wash, and dissolve in hydrochloric acid. Now boil the solution with a little **sulphurous acid**, to convert the **arsenate** into an **arsenite**. Having boiled off the sulphurous acid, pass **hydrogen sulphide**. The arsenic, originally present as an arsenate, is precipitated as **arsenic trisulphide**.

(*a*) $Mg(NH_4)AsO_4 + 3HCl = H_3AsO_4 + MgCl_2 + NH_4Cl$

(*b*) $H_3AsO_4 + SO_2 + H_2O = H_3AsO_3 + H_2SO_4$

(*c*) $2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O$

Filter off the arsenious sulphide, evaporate the solution to about half its bulk, and add excess of concentrated **nitric acid** and **ammonium molybdate**, when the phosphoric acid will be precipitated as yellow **ammonium phosphomolybdate** $12MoO_3(NH_4)_3PO_4$.

Arsenites do not give a precipitate with magnesia mixture, so should be tested for in the solution after the arsenate and phosphate have been precipitated and filtered off. By acidifying with hydrochloric acid, and passing hydrogen sulphide, a yellow precipitate of arsenic trisulphide is produced.

Pyrophosphoric and Metaphosphoric Acids.

When phosphoric acid is strongly heated, **pyrophosphoric acid** is produced. When disodium phosphate is heated, a sodium salt of pyrophosphoric acid is obtained.

$$(a) \quad 2H_3PO_4 = H_4P_2O_7 + H_2O$$
$$(b) \quad 2Na_2HPO_4 = Na_4P_2O_7 + H_2O$$

The **pyrophosphoric acid** is converted into **metaphosphoric acid** by heating more strongly, or better by heating it with phosphorus pentachloride.

$$(a) \quad H_4P_2O_7 = 2HPO_3 + H_2O$$
$$(b) \quad H_4P_2O_7 + PCl_5 = 2HPO_3 + POCl_3 + 2HCl$$

When boiled with water or dilute acids, both pyro- and meta-phosphoric acids are reconverted into orthophosphoric acid.

Metaphosphoric acid is generally called glacial phosphoric acid from its glass-like appearance; pyrophosphoric acid has also a vitreous appearance. **Metaphosphoric acid** coagulates **albumen** when shaken up with it, whereas neither ortho- nor pyrophosphoric acid possesses this property. **Silver nitrate** gives a white precipitate both with meta- and pyrophosphates. **Magnesium sulphate** in presence of ammonium chloride precipitates ortho- and pyrophosphates, but not metaphosphates.

Hypophosphorous Acid.

$$H_3PO_2 = H(H_2PO_2)$$

Hypophosphorous acid has only one hydrogen atom which is replaceable by metals; it is, therefore, a monobasic acid. All hypophosphites, with the exception of that of silver, are soluble in water.

Dry Reaction.—Hypophosphorous acid and hypophosphites, when heated, are converted into **phosphoric acid**, with liberation of **hydrogen phosphide (phosphine)**.

$$2H_3PO_2 = H_3PO_4 + PH_3$$

Wet Reactions.—Use a solution of sodium hypophosphite.

***1.** Hypophosphorous acid and its salts are very powerful reducing agents. On adding a solution of **copper sulphate** to an acidified solution of a hypophosphite and gently warming, a yellow precipitate of **cuprous hydride** is produced, which rapidly becomes chocolate-brown.

$$2H_3PO_2 + 2CuSO_4 + 3H_2O$$
$$= 2H_3PO_4 + H_2SO_4 + H_2SO_3 + Cu_2H_2$$

When treated with concentrated hydrochloric acid, cuprous hydride evolves hydrogen.

$$Cu_2H_2 + 2HCl = Cu_2Cl_2 + 2H_2$$

***2.** Salts of **mercury** are reduced to metallic mercury. This is sometimes employed for the quantitative determination of mercury compounds. In the case of mercuric chloride a white precipitate of calomel is first formed.

$$H_3PO_2 + 2HgCl_2 + 2H_2O = 2Hg + 4HCl + H_3PO_4$$

3. Silver nitrate gives with neutral solutions a white precipitate of silver hypophosphite, which is reduced to silver on boiling, with evolution of hydrogen.

$$NaH_2PO_2 + AgNO_3 = AgH_2PO_2 + NaNO_3$$
$$2AgH_2PO_2 + 4H_2O = 2H_3PO_4 + 2Ag + 3H_2$$

*4. **Neutral ammonium molybdate** gives, when added in excess, a beautiful blue coloration or precipitate. On boiling, the colour is destroyed.

*5. When exposed to the action of nascent hydrogen, by adding a piece of zinc to a solution of a hypophosphite acidified with hydrochloric acid, **hydrogen phosphide** is produced.

Detection of Free Phosphorus.—If free phosphorus is present in a mixture, it may be detected by (1) the smell; (2) mixing with a little water, adding excess of **tartaric acid,** and boiling. During the boiling hold two strips of paper in the neck of the flask, the one moistened with **silver nitrate,** the other with **lead acetate.** If the **silver nitrate** paper becomes brown or black, while the other does not, then the presence of phosphorus is shown. Should, however, both pieces be blackened, then hydrogen sulphide is present, and this, of course, masks the reaction given by phosphorus with the silver nitrate. Take another portion of the acidified mixture, and boil in a dark room, and the appearance of phosphorescence at the mouth of the flask proves the presence of phosphorus. (3) Mix the substance to be tested with **sulphuric acid** and **zinc** in a hydrogen-generating apparatus. As soon as all the air has been driven out of the apparatus ignite the issuing gas. If phosphorus is present, the flame assumes a pale yellowish-green tinge. The green tinge is much more marked if a white plate is depressed over the flame. (4) Shake up the substance under examination with a little **carbon disulphide** and pour off the aqueous solution. Now pour a few drops of the solution on a piece of filter paper; as the carbon disulphide evaporates, the phosphorus will be left on the paper in a state of very fine division. Should the quantity of phosphorus present be considerable, it will spontaneously ignite; or if the quantity is very small, it will merely show phosphorescence when examined in the dark.

Red phosphorus may be detected by (1) its insolubility in **solvents,** *i.e.* water, alcohol, caustic alkali, acids, etc.; (2) it ignites when heated, with formation of vapours of

phosphorus pentoxide; (3) on fusion with fusion mixture it forms a phosphate, which may be tested for with **ammonium molybdate.**

Boric Acid (Boracic Acid).

H_3BO_3

Most of the salts of boric acid are derived from **pyroboric acid,** $H_2B_4O_7$. The borates of the alkali metals dissolve in water, and have an alkaline reaction, this being due to the fact that boric acid is only very slightly ionised in solution. As none of the borates are quite insoluble in water, precipitation with reagents is never quite complete.

1. Most borates, when heated, swell up and fuse into a transparent glass.

2. Borates, when burnt on a filter paper moistened with cobalt nitrate, colour the ash blue. (*Cf.* Aluminium, p. 87.)

***3.** When a borate is mixed to a thin paste with concentrated **sulphuric acid,** and a little alcohol is added, the alcohol on being ignited burns with a green-edged flame. The green tinge is more noticeable on stirring with a glass rod. The green flame is produced by the burning of the volatile compound ethyl borate $B(OC_2H_5)_3$ produced in the reaction.

$$B(OH)_3 + 3C_2H_5OH \rightleftharpoons B(OC_2H_5)_3 + 3H_2O$$

Glycerol may be substituted for the sulphuric acid, in which case the mixture should be gently warmed before adding the alcohol and igniting.

N.B.—Metallic chlorides in presence of alcohol and sulphuric acid form **ethyl chloride,** which burns with a green flame. Again, copper salts on heating with concentrated sulphuric acid and alcohol may tinge the flame green. This is, however, not likely to occur if the mixture is not heated. Both these sources of error are minimised by using glycerol.

***4.** Grind up the dry substance with a little **sodium hydroxide,** or **potassium hydrogen sulphate,** and, by means of a platinum wire, heat in Bunsen flame. A transient green colour will be imparted to the flame.

5. **Silver nitrate** produces, in moderately dilute solutions, a white precipitate of **silver metaborate,** soluble in acids and in ammonia. On boiling the precipitate with water, reduction takes place, the precipitate turning brown, and then black.

$$Na_2B_4O_7 + 2AgNO_3 + 3H_2O = 2AgBO_2 + 2NaNO_3 + 2H_3BO_3$$

*6. On moistening **turmeric paper** with a slightly acid solution of a borate, and dried, it becomes reddish-brown. If the paper thus coloured be moistened with caustic soda the colour changes to a more or less greenish-brown shade. This reaction does not show so well in presence of ferric chloride, chromates, or chlorates.

*7. All borates are decomposed by **hydrofluoric acid** with formation of volatile **boric fluoride.** A mixture of sulphuric acid and calcium fluoride may be employed instead of hydrofluoric acid.

$$Na_2B_4O_7 + 6CaF_2 + 7H_2SO_4 = 6CaSO_4 + 4BF_3 + Na_2SO_4 + 7H_2O$$

Boric acid is volatile with steam or hydrochloric acid, and may be removed from a mixture by evaporating several times to dryness with hydrochloric acid; or, more expeditiously by evaporating, in a platinum or lead dish, with hydrofluoric acid.

8. **Drop Reaction.**—Boric acid in small quantities is not sufficiently acid to decolorise an alkaline solution of phenolphthalein. It does so, however, in the presence of a drop of glycerol.

Chromic Acid.

H_2CrO_4

The chromates and dichromates of the alkali metals are soluble in water, most of the other salts of these acids are insoluble.

*1. **Barium chloride** gives, with chromates or dichromates, a light yellow precipitate of **barium chromate,** soluble in mineral acids, but insoluble in acetic acid (distinction between barium and calcium).

$$K_2CrO_4 + BaCl_2 = BaCrO_4 + 2KCl$$
$$K_2Cr_2O_7 + 2BaCl_2 + H_2O = 2BaCrO_4 + 2KCl + 2HCl$$

*2. **Silver nitrate** produces a brick-red precipitate of **silver chromate,** soluble both in nitric acid and in ammonia, but insoluble in acetic acid.

$$K_2CrO_4 + 2AgNO_3 = Ag_2CrO_4 + 2KNO_3$$

*3. **Lead acetate** forms a yellow precipitate of **lead chromate.**

$$K_2CrO_4 + (CH_3COO)_2Pb = PbCrO_4 + 2CH_3COOK$$

It is soluble in excess of caustic alkali, forming a yellow solution,

$$PbCrO_4 + 4NaOH = Na_2PbO_2 + Na_2CrO_4 + 2H_2O$$

while on boiling with a small quantity of alkali, the precipitate changes from orange to chrome red.

4. **Hydrogen sulphide** or **sulphurous acid** turns the yellow or red solution green, owing to reduction to the green chromic salt. When hydrogen sulphide is employed, sulphur is precipitated.

(*a*) $2H_2CrO_4 + 3H_2S + 3H_2SO_4 = Cr_2(SO_4)_3 + 8H_2O + 3S$

(*b*) $K_2Cr_2O_7 + 3H_2SO_3 + H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O$

The chromium changes from the complex anion, in which it is present as CrO_4'' or Cr_2O_7'', to the green cation, where it occurs simply as the ion $Cr^{\cdot\cdot\cdot}$. In potassium chromate and potassium dichromate the ions are respectively $2H^{\cdot}$ and CrO_4'', and $2H^{\cdot}$ and Cr_2O_7'', whereas in chromium sulphate they are $2Cr^{\cdot\cdot\cdot}$ and $3SO_4''$. This explains why it is that only in chromium salts, where we have the cation $Cr^{\cdot\cdot\cdot}$, is chromium precipitated as hydroxide on addition of caustic alkali.

5. On heating with concentrated **hydrochloric acid,** chlorine gas is given off.

$$2K_2CrO_4 + 16HCl = 3Cl_2 + 2CrCl_3 + 8H_2O + 4KCl$$

*6. When chromates are heated with concentrated **sulphuric acid** and a **chloride**, deep red vapours of **chromyl dichloride** are produced, which condense to a heavy red liquid.

$$K_2Cr_2O_7 + 4NaCl + 3H_2SO_4 = 2CrO_2Cl_2 + 2Na_2SO_4 + K_2SO_4 + 3H_2O$$

Chromyl dichloride is decomposed, on mixing with water, into chromic and hydrochloric acids.

$$CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl$$

On adding ammonia to this solution, or on passing the vapours into dilute ammonium hydroxide, a solution of **ammonium chromate** is produced, which, on acidification with acetic acid and addition of lead acetate, gives a yellow precipitate of **lead chromate.**

This reaction may either be employed as a test for a chromate or indirectly as a test for a chloride, being of especial value when a chloride occurs in presence of a bromide. (*Cf.* Chlorides, p. 143.)

*7. **Hydrogen Peroxide.**—Acidify a very dilute solution of hydrogen peroxide with dilute sulphuric acid, add 3 to 4 c.c. of ether, and then a few drops of a dilute solution of a chromate or dichromate: a deep blue coloration is produced. On shaking up the mixture, the blue compound dissolves in the ether, forming a brilliant blue layer on the surface of the aqueous solution. This is a very delicate test for chromium. The coloration is probably due to formation of **perchromic acid.**

$$2H_2CrO_4 + H_2O_2 = 2HCrO_4 + 2H_2O$$

A large quantity of hydrogen peroxide should not be employed, neither should the chromic acid be in excess, because it decomposes the perchromic acid.

$$2HCrO_4 + 2H_2CrO_4 + 3H_2O = 4Cr(OH)_3 + 7O$$

The amount of the chromate to be added depends, therefore, upon the quantity of the hydrogen peroxide present, and it

should be added drop by drop with continual shaking. It is also advisable to add the ether before the chromate, because, when dissolved in ether, the colour is more permanent.

8. Drop Reaction.—See Chromium (§ 6, p. 91).

Permanganic Acid.

$HMnO_4$

This acid is known only in its aqueous solutions, and in the form of its salts, the **permanganates**, all of which are soluble in water, forming purple solutions.

***1.** Solid permanganates when heated to about 250° give off oxygen with formation of a green manganate.

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$$

***2.** Solid permanganates dissolve in concentrated **sulphuric acid**, forming a deep green solution. On gently warming, violet vapours of **manganese heptoxide**, Mn_2O_7, are given off, and, at the same time, oxygen mixed with ozone is evolved. These gases are probably produced by the decomposition of the heptoxide. If this experiment is conducted in a test-tube, it must be carried out with caution, because, when quickly heated, manganese heptoxide explodes.

$$2KMnO_4 + H_2SO_4 = Mn_2O_7 + K_2SO_4 + H_2O$$

The best way to show the formation of manganese heptoxide is to place a few small crystals of a permanganate in a porcelain basin, and then to moisten with concentrated **sulphuric acid**, when a green solution is formed. On now placing the dish on a water bath, violet vapours are given off, which condense on the upper parts of the basin, forming a violet film.

***3.** Solutions of permanganates evolve chlorine when warmed with concentrated hydrochloric acid.

$$2KMnO_4 + 16HCl = 5Cl_2 + 2MnCl_2 + 2KCl + 8H_2O$$

4. **Ammonium sulphide** gives a flesh-coloured precipitate of **manganese sulphide,** which usually has a yellowish appearance, owing to admixture with sulphur.

$$2KMnO_4 + 8(NH_4)_2S = 2MnS + 5S + K_2S + 8H_2O + 16NH_3$$

5. **Hydrogen peroxide,** when added to a solution of a permanganate which has been acidified with sulphuric acid, causes evolution of oxygen (volumetric method for determining hydrogen peroxide).

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = 5O_2 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

*6. All reducing agents decolorise solutions of permanganates, *e.g.* **hydrogen sulphide, ferrous sulphate, oxalic acid,** etc. If the solution is neutral or alkaline, a brown precipitate of hydrated manganese dioxide is produced.

(*a*) $$2KMnO_4 + 3H_2S = 2MnO_2 + 3S + 2KOH + 2H_2O$$

(*b*) $$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O$$

(*c*) $$2KMnO_4 + 5C_2H_2O_4 + 3H_2SO_4 = 10CO_2 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

Manganese is not precipitated from solutions of permanganates by the usual reagents, caustic alkalis, etc., because the manganese is present in the complex anion MnO_4'. Potassium permanganate, *e.g.*, is dissociated in aqueous solution into the ions $K^\cdot$ and MnO_4'. As soon as reduction takes place, the manganese becomes the cation, and the colour of the solution changes from intense purple to colourless or light pink, *e.g.* $MnSO_4$, which is ionised into the ions $Mn^{\cdot\cdot}$ and SO_4''. Manganese sulphide is indeed precipitated from a permanganate on addition of ammonium sulphide, the explanation of this apparent anomaly being that the ammonium sulphide first reduces the permanganate to a manganese salt. The salts of H_2MnO_4 are green, and contain the divalent anion

MnO_4''. They are called **manganates**. The permanganates contain the monovalent anion MnO_4', and are purple.

Chloric Acid.

$HClO_3$

Chloric acid is only known in aqueous solution and in the form of its salts. The chlorates are all soluble in water.

1. The chlorates are decomposed on heating, with evolution of oxygen gas; *e.g.*—

$$2KClO_3 = KCl + KClO_4 + O_2$$

*2. Concentrated **sulphuric acid** when added to a solid chlorate is coloured yellow, owing to the liberation of **chlorine dioxide.** If the mixture is warmed an explosion ensues, therefore only very small quantities should be taken.

$$3KClO_3 + 2H_2SO_4 = 2ClO_2 + 2KHSO_4 + KClO_4 + H_2O$$

3. On adding concentrated **hydrochloric acid** to a solution of a chlorate, the mixture becomes coloured yellow, and chlorine is evolved.

$$KClO_3 + 6HCl = 3Cl_2 + KCl + 3H_2O$$

*4. **Silver nitrate** produces no precipitate with chlorates, because silver chlorate is readily soluble. If, however, the chlorate is first boiled with a little sulphurous acid, so as to reduce it to a chloride, a white precipitate of **silver chloride** is obtained.

$$KClO_3 + 3SO_2 + 3H_2O = KCl + 3H_2SO_4$$

Chlorates give no precipitate of silver chloride with silver nitrate, because the chlorine is present in the form of a complex anion: potassium chlorate, for example, when in aqueous solution is ionised into the ions $K^{\cdot}$ and ClO_3' and silver chlorate into $Ag^{\cdot}$ and ClO_3'.

Perchloric Acid.

$HClO_4$

Potassium perchlorate is formed when potassium chlorate is heated. (See § 1, above.) The free acid is obtained by distillation of the potassium salt with acid. It forms hydrates containing one or two H_2O molecules, but in the pure state it is *highly explosive* especially in contact with organic matter. Solutions in water are ionised and are therefore safe.

Dry Reactions.—(1) Perchlorates are decomposed by ignition in the dry state with an ammonium salt.

$$3NaClO_4 + 8NH_4Cl = 3NaCl + 4N_2 + 8HCl + 12H_2O$$

This is the best method for removing perchlorates from a mixture.

(2) When fused with a chloride, chlorine is evolved.

Reactions in Solution.—**1. Silver nitrate** produces no precipitate.

2. Potassium or **ammonium sulphate** precipitates the corresponding perchlorate; both are white and crystalline and are insoluble in alcohol.

3. Reduction.—Zinc dust is without effect (compare nitrates), but titanium trichloride reduces perchlorates to chlorides.

Bromic Acid.

$HBrO_3$

This acid is only known in aqueous solution and in the form of its salts. Most bromates are soluble in water.

1. On strongly heating, the alkali bromates are converted into bromides, with evolution of oxygen.

$$2KBrO_3 = 2KBr + 3O_2$$

Other bromates decompose with evolution of bromine and oxygen.

$$Mg(BrO_3)_2 = MgO + Br_2 + 5O$$

*2. **Silver nitrate** produces a white, beautifully crystalline precipitate of **silver bromate**, which is with difficulty soluble in nitric acid, but readily soluble in ammonia.

$$KBrO_3 + AgNO_3 = AgBrO_3 + KNO_3$$

3. **Mercurous nitrate** produces a white precipitate of **mercurous bromate.**

$$2KBrO_3 + 2HgNO_3 = Hg_2(BrO_3)_2 + 2KNO_3$$

4. Mineral acids decompose bromates with liberation of free **bromine,** bromic acid being first liberated, which then slowly decomposes into hydrobromic acid and oxygen. The hydrobromic acid then acts on the bromic acid, thus—

$$HBrO_3 + 5HBr = 3Br_2 + 3H_2O$$

*5. **Hydrogen sulphide** or **sulphur dioxide** reduces bromates to bromides.

(*a*) $KBrO_3 + 3H_2S = KBr + 3H_2O + 3S$

(*b*) $KBrO_3 + 3SO_2 + 3H_2O = KBr + 3H_2SO_4$

Iodic Acid.

HIO_3

Iodic acid is a colourless crystalline solid decomposed at 170°. The alkali iodates are readily soluble in water, but most of the other iodates only with difficulty.

1. On heating, the alkali iodates are converted into iodides with evolution of oxygen.

$$2KIO_3 = 2KI + 3O_2$$

*2. Concentrated **sulphuric acid** only decomposes iodates after addition of a solution of ferrous sulphate or other reducing agent.

(*a*) $HIO_3 + 3H_2SO_4 + 6FeSO_4 = HI + 3H_2O + 3Fe_2(SO_4)_3$

(*b*) $HIO_3 + 5HI = 3I_2 + 3H_2O$

*3. **Silver nitrate** gives a white curdy precipitate of **silver iodate.**

$$KIO_3 + AgNO_3 = AgIO_3 + KNO_3$$

It is soluble with difficulty in nitric acid, but readily soluble in ammonia. From its ammoniacal solution **sulphur dioxide** precipitates yellow silver iodide.

$$AgIO_3 + 3SO_2 + 3H_2O = AgI + 3H_2SO_4$$

4. **Barium chloride** produces a white precipitate of **barium iodate** soluble with difficulty in dilute nitric acid.

$$2KIO_3 + BaCl_2 = Ba(IO_3)_2 + 2KCl$$

*5. **Mercurous nitrate** gives a light yellow, curdy precipitate of **mercurous iodate.**

$$KIO_3 + HgNO_3 = HgIO_3 + KNO_3$$

*6. **Hydrogen sulphide** or **sulphur dioxide** reduces iodates with the formation of iodides.

(*a*) $$KIO_3 + 3H_2S = KI + 3H_2O + 3S$$

(*b*) $$KIO_3 + 3SO_2 + 3H_2O = KI + 3H_2SO_4$$

*7. Iodine is liberated from a solution containing a strong acid, an iodate, and an iodide.

$$6HCl + KIO_3 + 5KI = 3H_2O + 3I_2 + 6KCl$$

This reaction is used in volumetric analysis to determine iodates, iodides or acids. Potassium iodide is added to the solution of an iodate which is then acidified with dilute hydrochloric acid, and the iodine liberated is titrated.

Hydrogen Peroxide.

$$H_2O_2$$

Use a solution of hydrogen peroxide, or dissolve a little sodium peroxide in water, care being taken to keep it cool while solution is taking place.

***1. Chromic Acid.**—To a solution of hydrogen peroxide containing dilute sulphuric acid, add about 3 c.c. of ether and two or three drops of potassium dichromate, and shake up. A deep blue coloration is obtained which dissolves in the ethereal layer. This reaction only shows satisfactorily when both the hydrogen peroxide and the potassium dichromate are very dilute. (*Cf.* § 7, p. 184.)

***2. Potassium Ferricyanide and Ferric Chloride.**—Mix very dilute solutions of ferric chloride and potassium ferricyanide, when a light brown coloration is produced. Now add a few drops of a dilute solution of hydrogen peroxide. The solution gradually becomes green, and in a short time Prussian blue is precipitated out. This is a very delicate reaction; it depends on the reduction by the hydrogen peroxide of the ferricyanide to ferrocyanide, and is an example of reduction by an oxidising agent.

(*a*) $2K_3Fe(CN)_6 + H_2O_2 = 2K_3HFe(CN)_6 + O_2$

(*b*) $3K_3HFe(CN)_6 + 4FeCl_3 = Fe_4[Fe(CN)_6]_3 + 9KCl + 3HCl$

***3. Potassium Iodide.**—On addition of hydrogen peroxide to a solution of potassium iodide which has been acidified with dilute sulphuric acid, iodine is liberated.

$$2HI + H_2O_2 = I_2 + 2HOH$$

The addition of a small quantity of starch paste makes the reaction exceedingly delicate.

***4. Hydrogen Auri-chloride.**—In alkaline solution salts of gold are reduced, and finely-divided gold is precipitated. The solution assumes a greenish or brownish-purple appearance.

$$2HAuCl_4 + 3H_2O_2 + 8NaOH = 2Au + 8NaCl + 3O_2 + 8H_2O$$

5. Titanium sulphate (prepared by heating titanium dioxide in strong sulphuric acid, cooling, diluting, and filtering) produces a golden-yellow colour, due to pertitanic acid (sometimes written TiO_2, H_2O_2. (See § 6, p. 114.)

$$Ti(SO_4)_2 + H_2O_2 + 2H_2O = 2H_2SO_4 + H_2TiO_4.$$

Addition of an alkali produces a yellow-orange precipitate, which is soluble in excess.

6. Drop Reaction.—Add a strong solution of potassium carbonate to some cerous sulphate solution until the white precipitate formed re-dissolves, and add a drop of the fresh resulting mixture to the solution to be tested. A red-brown colour is produced in the presence of more than 0·001 mgrm. of hydrogen peroxide owing to the formation of potassium perceric carbonate.

Hydroxyl Ion.

OH'

Solutions containing an excess of hydroxyl ions over hydrogen ions are alkaline, and will turn red litmus blue, methyl orange yellow, and yellow turmeric brown.

***1. Phenolphthalein.**—A red solution is obtained when a solution of phenolphthalein is added to a solution containing an appreciable excess of free hydroxyl ions.

***2. Ferric Chloride.**—On the addition of ferric chloride to a solution containing hydroxyl ions, a brown precipitate of ferric hydroxide is produced.

$$Fe^{\cdot\cdot\cdot} + 3OH' = Fe(OH)_3$$

Solutions of many other metallic salts behave in a similar manner, *e.g.* aluminium sulphate gives a white gelatinous precipitate; copper sulphate a greenish precipitate which turns black on boiling.

$$(a)\quad Al^{\cdot\cdot\cdot} + 3OH' = Al(OH)_3$$
$$(b)\quad Cu^{\cdot\cdot} + 2OH' = Cu(OH)_2$$

It must be remembered that although the alkalinity of a solution is due to hydroxyl ions, it may not be due to the presence of an hydroxide. For example, a solution of sodium carbonate is strongly alkaline, the alkalinity being due to

hydrolysis (see p. 17). A solution of potassium cyanide is likewise markedly alkaline (see p. 151), the alkalinity in this case also being due to hydrolysis. In both of these cases, besides giving the reactions for the hydroxyl ion, the solutions will give the reactions, respectively, for carbonates and cyanides. (For detection of hydroxyl in presence of carbonates, see p. 228.)

CHAPTER X.

ANALYTICAL TABLES FOR THE DETECTION AND SEPARATION OF THE METALLIC RADICALS (CATIONS) AND ACID RADICALS (ANIONS).

Preliminary Examination of the Substance to be Analysed.

A. Heat a small portion of the dried and powdered substance in an ignition tube.

(*a*) The substance chars → organic matter.

(*b*) ,, ,, melts → fusible salts (*e.g.* alkali salts), some oxides, or salts containing much water of crystallisation.

(*c*) The substance swells up → alums, borates, or $Hg(CNS)_2$.

(*d*) ,, ,, changes in colour. These colour changes may be the result of complex double decomposition between substances occurring together, or they may be characteristic changes of the simple substance. Some examples of the common colour changes are noted below.

1. Physical changes of oxides :—

Cold.	Hot.	Oxide.
Light yellow	Yellowish-brown, does not fuse	SnO_2
White	Yellow, does not fuse	ZnO
Yellow	Dark brown, fuses	PbO
Lemon-yellow	Orange, fuses	Bi_2O_3
Red	Black, on strong heating forms globules of mercury	HgO
Red	Black, fuses on further heating, becoming yellow at the points of fusion	Pb_3O_4
Rusty red	Black-red, does not fuse	Fe_2O_3

2. Some sulphides undergo similar changes.

3. Dehydration of crystalline salts :—

Hydrated.	Anhydrous.	Substance.
Blue or green	White or olive	Some cupric salts
Green	Dirty white or yellow	Some nickel and iron salts
Pink	Blue or violet	Some cobalt salts

4. Changes of colour due to decomposition.—The nitrates and carbonates of the heavy metals leave their oxides as residues ; *e.g.*—

Original substance.	Residue.
Nitrates of mercury, colourless	Red HgO
Cupric nitrate, blue	Black CuO
Cupric carbonate, light green	Black CuO
Cobalt nitrate, pink	Black Co_2O_3
Nickel nitrate, green	Black Ni_2O_3
Ferrous sulphate, green	Red Fe_2O_3
Lead nitrate, colourless	Yellow PbO
Lead carbonate, white	Yellow PbO

5. The substance evolves vapours which are coloured :—

Brown . .	(*a*) Chromyl chloride from admixture of **chloride** and **chromate**. (*b*) Oxides of nitrogen from some **nitrates** and **nitrites**. (*c*) Bromine from some **bromides** and **bromates**.
Greenish-yellow.	Chlorine from **chlorides** of gold, platinum, copper, etc.
Violet . .	Iodine from some **iodides** and **iodates**.
White fumes .	(*a*) Steam from water of crystallisation. (*b*) Hydrogen chloride from some **chlorides**. (*c*) Sulphur trioxide from certain **sulphates**. (*d*) Volatilisation of certain **ammonium salts**.

5*a*. The gas evolved is colourless and odourless :—

Oxygen . .	Rekindles a glowing chip of wood, from readily decomposed **oxides, peroxides, chlorates**, and **nitrates**.
Nitrous oxide .	Rekindles a glowing chip of wood, from **ammonium nitrate**. Steam will also be evolved.
Carbon dioxide .	Turns lime-water turbid, from **carbonates** and **oxalates**, or admixture of carbon with oxidising agents.
Carbon monoxide	Burns with blue flame, from **oxalates** and other **organic salts**.

5b. Gas is colourless with smell :—

Sulphur dioxide	Smells of burning sulphur, from **thiosulphates, sulphites,** some **sulphates,** and from admixture of sulphides with oxidising agents.
Cyanogen . .	Burns with purple flame, from **cyanides** of the heavy metals.
Ammonia . .	Characteristic odour, and turns red litmus blue, from some **ammonium salts** and certain organic substances ; *e.g.* **urea.**
Hydrogen phosphide . .	Odour of rotten fish, burns with a greenish flame, from **hypophosphites.**

6. A sublimate is formed :—

White.	Coloured.	Black.
Ammonium, mercury, arsenic and antimony compounds, beside some organic acids ; *e.g.* benzoic, oxalic, etc.	**Yellow :** while hot, brownish drops of liquid, **sulphur**	**Arsenic, antimony,** either in the free state or from being set free by action of reducing agents occurring in mixture
Examples, NH_4Cl, readily soluble in water	**Yellow :** becomes red on being rubbed, HgI_2	Black, becoming red on rubbing, HgS
Hg_2Cl_2, Hg_2Br_2, insoluble in water	**Yellow :** brownish-red while hot. As_2S_3	Grey, cohering to globules on rubbing, Hg
$HgCl_2$, $HgBr_2$, soluble in water	**Orange :** almost black while hot, Sb_2S_3	Black crystalline, soluble in carbon tetrachloride to a purple solution. **Iodine**
As_4O_6 octahedral crystals		
Sb_4O_6 needle-shaped crystals, not so readily volatile as As_4O_6		

When a **white sublimate** is obtained, a small quantity of the substance should be mixed with twice its bulk of soda-lime, and heated in a test-tube. If mercury is present, a mirror and globules of Hg will be produced on the cool part of the tube. A black mirror of arsenic is formed when arsenic compounds are present. A smell of ammonia points to the presence of ammonium salts.

B. Heat some of the substance in a "draught tube" (a glass tube open at both ends) :—

<table>
<tr><td colspan="2">(*a*) Sulphur and the sulphides of the heavy metals yield SO_2, while free sulphur may escape oxidation more or less and appear as a sublimate. The sulphides yield residues or sublimates of metals, oxides, or oxysulphides. Examples :</td><td rowspan="3">(*b*) Carbon will be burnt off as CO_2
(*c*) Some metals will be oxidised ; *e.g.* As, Sb, Mg, etc. Some of these yield sublimates. Other changes will go on as in the closed ignition tube</td></tr>
<tr><td>Metals.</td><td>Oxides.</td></tr>
<tr><td>(1) Ag—residue from Ag_2S
(2) Hg—sublimate from HgS</td><td>(1) ZnO—residue from ZnS
(2) As_4O_6—sublimate from As_2S_3
(3) Sb_4O_6—sublimate from Sb_2S_3</td></tr>
</table>

C. Heat a small portion of the substance in a tube with about three times its bulk of powdered soda-lime, or fusion mixture and potassium cyanide. **Arsenic** or **antimony,** if present, will form a black mirror on the sides of the tube ; **mercury** a grey mirror, which on rubbing with a match will cohere in globules.

D. Heat a trace of the substance in the Bunsen flame on an asbestos thread, at the same time holding a porcelain basin over it as described under "Film Reactions," p. 7. If a film is produced, examine it according to the table on next page.

E. **Flame Test.**—Heat a little of the substance on a platinum wire in the Bunsen flame. First, however, moisten the wire with concentrated hydrochloric acid (p 8) :—

Flame colour.	Flame colour through blue glass.	Element.
1. Golden-yellow	1. —	1. Sodium
2. Violet	2. Violet-red	2. Potassium
3. Dull red	3. Greenish-grey	3. Calcium
4. Crimson	4. Purple	4. Strontium
5. Bluish-crimson	5. Purple	5. Lithium
6. Yellowish-green	6. Bluish-green	6. Barium
7. Green	7. —	7. Boric acid, copper, phosphates
8. Pale blue	8. —	8. Copper, arsenic, antimony, bismuth, lead, cadmium, zinc

TABLE OF FILM REACTIONS.

Metallic film.	Oxide film.	HI on oxide films.	Iodide film when breathed upon.	$(NH_4)_2S$ on oxide film.	Bleaching powder solution on metallic film.	Element.	Remarks.
Black, edges brown, slowly soluble in 20 % HNO_3	White	Orange to salmon pink	Disappears, but returns again	Orange, dissolves in $(NH_4)_2S$, reappears on gently warming	No action	Sb	The oxide film on moistening with a drop of $AgNO_3$ and NH_4OH turns black
Black, edges brown, almost insoluble in 20 % HNO_3	White	Yellow	Disappears, but returns again	Yellow, dissolves in $(NH_4)_2S$, reappears on gently warming	Immediately dissolves	As	The oxide film when moistened with a drop of $AgNO_3$ and NH_4OH turns yellow
Black, edges brown, dissolves at once in 20 % HNO_3	White	Canary-yellow	Disappears, but reappears again	Reddish-brown, dissolves in $(NH_4)_2$, reappears on warming	No action	Sn	
Black, with brown edges, slowly soluble in 20 % HNO_3	White with a yellowish tinge	Brownish-pink	Disappears, but only very slowly reappears	Brownish-black	No action	Bi	
Grey, has a mottled appearance, slowly soluble in 20 % HNO_3	None	HI on metallic film. Scarlet, or yellow, which becomes scarlet slowly	No change	Black [$(NH_4)_2S$ on metallic film]	No action	Hg	
Black, edges brown, dissolves at once in 20 % HNO_3	Very pale yellow	Bright yellow	No change	Black	Dissolves, and then turns brownish-yellow	Pb	
Black, edges light brown, dissolves at once in 20 % HNO_3	Brown	White	No change	Light yellow, does not dissolve in $(NH_4)_2S$	No change	Cd	

F. Examine the coloured flame through the spectroscope and compare the spectra with the illustration at the commencement of the book (see p. 9).

G. Apply the **Match Test** (see p. 6) :—

Appearance of metallic bead.	Metal.
1. White, readily cut with a knife, marks paper	Lead
2. White and brittle	Antimony, bismuth
3. White, moderately soft	Silver
4. Red flakes, not usually a bead	Copper
5. Yellow flakes	Gold
6. Dark grey powder, which is magnetic	Iron, nickel, cobalt

Separate the magnetic powder (Match Test 6, above) from adhering carbon by means of a magnet or magnetised knife blade. Place any adhering particles upon a filter paper, and moisten with a drop each of dilute hydrochloric and nitric acids. Dry gently over the flame, faint pink turning blue—**cobalt**; greenish stain turning yellow—**nickel**; add a drop of potassium ferrocyanide to the stain, a deep blue coloration produced—**iron.**

The metallic bead should always be dissolved in nitric or hydrochloric acid, and wet tests applied, as much information can thus be obtained.

H. **Borax Bead Test** :—

Reducing flame.	Oxidising flame.	Element.
1. Sapphire blue	1. Sapphire blue	Cobalt
2. Red. (This may be more readily obtained by adding a trace of stannous chloride to the bead)	2. Blue on cooling, greenish while hot	Copper
3. Green	3. Green	Chromium
4. Yellowish-brown, often grey from specks of metallic nickel	4. Yellowish-brown	Nickel
5. Yellow while hot, bottle-green on cooling	5. Yellow while hot, bottle-green on cooling	Iron
6. Colourless	6. Amethyst violet	Manganese

I. **Test for Ammonium Compounds.**—A little of the substance is boiled in a test-tube with caustic soda. If a smell of ammonia is produced, and if a piece of moist red litmus paper held in the mouth of the tube be turned blue, presence of ammonium compounds is shown. If the vapours coming from the test-tube are brought near an open bottle of hydrochloric acid, dense white fumes of ammonium chloride result. (See also § 2, p. 132.)

J. **Test for Manganese and Chromium.**—Mix a little of the substance with fusion mixture and a trace of sodium nitrate. Take up a portion of the mixture on a small loop at the end of a piece of platinum wire and fuse in the oxidising flame of the Bunsen burner. A green mass shows **manganese** to be present. A yellow one shows the presence of **chromium.** If the two metals occur together, the green colour of the manganate obscures the yellow colour of the chromate. To test for chromium in the presence of manganese, dissolve the bead in water, add a few drops of alcohol, warm and filter. Acidify the filtrate with acetic acid and add **silver nitrate**; a red precipitate or coloration shows that chromium is present. (See also § 7, p. 92.)

Preliminary Examination for Acids.

I. To a small portion of the substance add **dilute sulphuric acid,** and warm.

Vapours are coloured.	Vapours colourless and odourless.	Vapours colourless and have an odour.
1. Reddish - brown vapours of NO_2, **nitrite.** Confirm by §§ 1 or 6, pp. 163, 164.	1. Effervescence takes place. Hold a glass rod which has been moistened with lime-water in the mouth of the test-tube. A white film of calcium carbonate is formed on the rod: **carbonate.**	1. Smell of burning sulphur: **sulphites.**
2. Reddish - brown vapours of bromine. Presence of **bromide** and **bromate** together.	2. Hydrogen from action of certain metals on sulphuric acid.	2. Smell of burning sulphur with precipitation of sulphur: **thiosulphate.**
3. Greenish-yellow, chlorine from **hypochlorites.** Confirm by adding **lead acetate** (§ 3, p. 150) to the solution as prepared on p. 224.	3. Oxygen from peroxides or persulphates.	3. Smell of rotten eggs. Gas evolved turns lead paper black and nitro-prusside paper violet: **sulphide.**
4. Violet vapours of iodine. Presence of both **iodide** and **iodate.**	4. Hydrogen peroxide from true **per-acids.**	4. Smell of bitter almonds. Hold a glass rod moistened with silver nitrate in mouth of test-tube; white coating of silver cyanide: **cyanide, ferrocyanide, ferricyanide.**
		5. Vapours have a pungent acid smell. **Formate, acetate.**

II. Add **concentrated sulphuric acid** to a small portion of the substance, and heat. Do not, however, heat to boiling, otherwise vapours of sulphuric acid will be given off which make it difficult to recognise the vapours of other acids.

Vapours are coloured.	Vapours colourless and odourless.	Vapours colourless but have an odour.
1. Brown vapours: bromine from **bromides** or **bromates**; chromyl chloride from **chromates** in presence of **chlorides**; nitrogen peroxide from **nitrites**, and in certain circumstances from **nitrates**. The bromine and chromyl chloride condense on the sides of the test-tube to a brown liquid.	1. Oxygen gas evolved which supports combustion: **peroxide, manganate, chromate,** etc.	1. **Hydrogen sulphide, sulphur dioxide** (either from a sulphite, or by action of reducing agents on sulphuric acid), and **acetic acid** may be obtained. (See 1, 2, and 4, p. 202.)
2. Very light brown vapours: **nitrates**. Confirm by heating with sulphuric acid and a piece of copper foil. Dark brown vapours will be evolved if a nitrate is present.	2. Carbon monoxide which burns with a blue flame: **formate, oxalate, cyanide, ferrocyanide,** and **ferricyanide.**	2. White fumes: **fluoride.** Confirm by heating with a little sand and concentrated sulphuric acid, and holding a moist glass rod in the mouth of the test-tube. The glass rod will, if a fluoride is present, become coated with a white film of silicic acid.
3. Violet vapours condensing to shining crystals: **iodide.** 4. Violet vapours of Mn_2O_7, which do not form crystals: **permanganate.** 5. Greenish-yellow vapours of chlorine dioxide, accompanied by slight explosion: **chlorate.** 6. Chlorine from hypochlorites and from chlorides in presence of peroxides.	3. Carbon dioxide from **carbonates, oxalates,** and other organic acids. The presence of organic acids is usually accompanied by charring, and consequent evolution of sulphur dioxide.	3. White fumes: **hydrochloric acid, hydriodic acid, hydrobromic acid.** Hydrobromic and hydriodic acids are usually accompanied by fumes of bromine or iodine.

Treatment of the Substance to be Analysed.

I. The Substance is a Liquid.

(*a*) A few drops should be evaporated to dryness on a piece of platinum foil. If no residue is left, and if the liquid is neutral to litmus paper and has no odour, it is probably **water.**

(*b*) If, on evaporating to dryness, a residue is left which, on further heating, chars, then **organic matter** is present, and must be eliminated before analysing for them etals. (See p. 207.) If there is no organic matter, proceed at once to test for bases and acids (cations and anions). The odour and colour of the solution will often give very useful information.

(*c*) Test the solution with litmus paper; if it is **alkaline,** this may be due to the presence of hydroxides, alkali carbonates, peroxides, cyanides, borates or sodium salts of aluminium, or of zinc. Test for peroxides (p. 190), carbonates (p. 158), hydroxides (p. 192), and ammonium (p. 131). If the solution has an acid reaction, free acids or acid salts may be present.

II. The Substance is a Solid.

The solid must be finely powdered, and a small portion, **in no case the whole of the substance,** should be treated with—

(*a*) **Water,** first cold and then boiling. If it dissolves, proceed at once with analysis. If it appears to be insoluble, filter and evaporate a few drops of the filtrate to dryness on platinum foil or on a watch-glass. A residue indicates that a portion has dissolved.

(*b*) Treat the **undissolved** portion with dilute **hydrochloric acid,** and boil. If it does not dissolve, add strong hydrochloric acid, and again boil. It may be necessary to boil for some minutes, because such substances as Fe_2O_3 or MnO_2 only dissolve on continued boiling. In any case, should chlorine be evolved, the boiling must be continued till the gas is no

longer given off, because the evolution of chlorine proves that a reaction is taking place. If the substance appears not to dissolve, add about 3 volumes of water to the mixture, and boil; solution may then take place. For example, when stannic oxide is boiled with hydrochloric acid, a chloride $Sn_5O_5Cl_2(OH)_8$ is produced; this is insoluble in strong hydrochloric acid, but dissolves on addition of water. Again, on treating potassium antimonate or potassium arsenate with hydrochloric acid, solution is not readily obtained, but on dilution and boiling a clear solution is produced. The dry reactions are very useful guides how to obtain solution.

(*c*) If it is insoluble in hydrochloric acid, boil another small portion with **aqua regia** (3 parts conc. HCl, 1 part conc. HNO_3).

Treatment of Substance in Solution.

A. *The Aqueous Solution.*—Add dilute **hydrochloric acid,** and go through the group separations.

B. *The Hydrochloric Acid Solution.*—Pass or add **hydrogen sulphide** to the hot solution, and go through the group separations.

C. *A Portion of the Substance is soluble in Water, and another Portion in Hydrochloric Acid.*—If on adding a drop of **hydrochloric acid** to the aqueous solution no precipitate is produced, the two portions may be mixed. If a precipitate is produced, add hydrochloric acid until precipitation is complete. Filter off, and examine the residue for metals of the **silver group.** The acidic filtrate and the aqueous solution may then either be mixed or analysed separately. Generally speaking it often saves trouble and complications to analyse them separately, because each solution may only contain one substance; also a precipitate may be produced on adding the aqueous solution to the hydrochloric acid solution, even if the metals of the **silver group** are absent. This may be due to the formation of the **oxychlorides** of bismuth, antimony, or

tin. In such a case pass hydrogen sulphide without filtering, so that the finely-divided oxychlorides will be converted into sulphides. The two solutions should not be mixed until the aqueous solution has been tested for metals of the **silver group.**

D. *The Solution in Aqua Regia.*—Evaporate nearly to dryness. Add a little concentrated hydrochloric acid, and again evaporate to small bulk, in order to get rid of the last traces of nitric acid, which would cause precipitation of sulphur on passing hydrogen sulphide through the solution.

Now dissolve the residue in hot water, adding a little hydrochloric acid, if necessary, to redissolve bismuth, antimony, and tin oxychlorides.

E. When a powder does not apparently dissolve in **hydrochloric acid,** it is difficult sometimes to say whether the substance was originally insoluble in acid, or whether it has been converted into an **insoluble chloride.** Should this difficulty arise, treat a small portion of the original substance with **nitric acid,** and add a few drops of hydrochloric acid to the solution. If the metals of the **silver group** are present, a white precipitate will be produced. In this case treat a larger quantity of the substance in the same manner, and, after filtering off the precipitate, employ the solution for the analysis of the succeeding groups after the removal of nitric acid as described in the preceding paragraph. Analyse the residue for the silver group.

Treatment of Substances Insoluble in Acids.

The chief substances insoluble in **water** and in **hydrochloric acids** are the halogen salts of **silver** and mercurous mercury, the sulphates of **barium, strontium,** and **lead, mercuric** sulphide, **stannic** oxide, **calcium** fluoride, ignited oxides such as Al_2O_3, SnO_2, Sb_2O_3, Cr_2O_3, and fused $PbCrO_4$.

Aqua regia will not dissolve the halogen salts of silver (in fact, aqua regia converts silver salts into insoluble silver chloride), ignited Cr_2O_3, Al_2O_3, or fused $PbCrO_4$; neither will

it attack the sulphates of **barium** and **strontium** ; SiO_2 is also insoluble. CaF_2, although insoluble in aqua regia, can be decomposed with concentrated sulphuric acid.

The dry reactions should indicate whether any of these substances are present in a mixture, and should therefore act as a guide for the treatment of the insoluble portion.

For example, all the silver salts are readily reduced, and small beads of the metal can be obtained by means of the match test. Lead and tin can also be obtained as metal. The beads may be dissolved in nitric acid and tested in the wet way. Sulphates, when heated on charcoal, are easily reduced to sulphides. (See p. 165.)

I. The sulphates of barium and strontium, and oxides such as Al_2O_3, Cr_2O_3, Sb_2O_3, and SnO_2, are most conveniently brought into solution by fusing the solid substance with three times its weight of dry fusion mixture in a silver, platinum, or porcelain crucible.† The addition of a small quantity of sodium peroxide causes the reaction to take place at a lower temperature. When the fused mass forms a clear fluid, it is cooled and the melt boiled with distilled water. The residue, if any, is filtered off. In the case of the metals barium and strontium, it consists of the carbonates of these metals. In the other cases cited, the metal is contained in the solution as sodium chromate, sodium antimonate, etc.

II. (*a*) Insoluble **silicates**. Supposing it is required to analyse glass, porcelain, or other silicates, they can be brought into a condition for analysis by fusion as already described for the sulphates. Sodium silicate, which is soluble in water, is produced ; aluminium would also be converted into the soluble sodium aluminate, whereas iron would remain as a residue when the melt is treated with water. The **solution,** after acidifying with hydrochloric acid, is evaporated to dryness, when the silica is obtained as insoluble SiO_2, and on extracting with dilute hydrochloric acid is left behind.

† Nickel may also be used, but in this case usually a small amount of nickel will be found in the melt. Silver is really the most satisfactory.

(*b*) Or the silicate may be heated with hydrofluoric acid in a platinum dish, when the silica is converted into silicon tetrafluoride, which is driven off on heating.

III. Insoluble **tin** compounds, such as native tin stone, are best converted into the soluble condition by **fusion with sulphur and sodium carbonate.** Mix the dried substance with five or six times its weight of a mixture of equal parts of sulphur and dry sodium carbonate. Place in a crucible and put on the lid; now heat over a *small* Bunsen flame until all the sulphur has burned off. On cooling, treat the melt with hot water and filter. The insoluble portion may consist of the sulphides of other metals which do not form thio-compounds. The tin is obtained in the form of sodium thio-stannate—

$$2SnO_2 + 2Na_2CO_3 + 9S = 2Na_2SnS_3 + 3SO_2 + 2CO_2$$

Insoluble **halogen salts,** which can only be silver salts, may be decomposed by bringing them in contact with zinc in presence of dilute sulphuric acid.

$$Zn + 2AgCl = 2Ag + ZnCl_2$$

The metallic silver is filtered off and washed with a little water; it can then be dissolved in nitric acid, and tested as usual. The solution is tested for the halogen acid.

Elimination of Organic Matter.—Organic matter need not, as a rule, be removed until after the precipitation of the metals of the **copper group.** Large quantities of tartaric or oxalic acids interfere, however, with the precipitation of tin. If this metal is present, these acids should be removed before passing H_2S.

To remove the organic matter the substance is evaporated to dryness and ignited at a low temperature, thus charring and destroying most organic materials. Oxalates do not char, but are converted into carbonates or oxides. When thoroughly charred the residue is dissolved in water or dilute hydrochloric acid. The solution is then filtered from charcoal and examined, as usual.

If it is necessary to remove the organic matter before commencing analysis for the metals of the silver and copper groups, the substance may be ignited as above. But should **mercury, arsenic,** or **antimony** be present such a proceeding is inadmissible, because of these metals and their salts are volatile. In presence of these metals the following method should be employed: Place the substance in a small heat-resistant flask with a long neck (a micro-Kjeldahl flask), add a few c.c. of perchloric acid, and heat on the water bath (not over a flame) in the fume cupboard. While the liquid is hot add cautiously (holding the mouth of the flask away from the face) a few drops of nitric acid, and warm over a flame until no more red fumes result. Repeat the treatment until no more charred matter is present, and finally evaporate to dryness. Now add about 5 c.c. of concentrated hydrochloric acid, and evaporate to a pasty consistency. Dissolve in water, and analyse as usual. If the metals of the silver group are present, the chlorides formed will not dissolve in water. By this treatment any arsenic which may have been present will have been converted to the higher state of oxidation. The solution, therefore, must be reduced by boiling with sulphurous acid until the odour of sulphur dioxide is no longer apparent, before passing or adding hydrogen sulphide.

III. The Substance appears Metallic.

(*a*) Treat a small portion of the substance with dilute hydrochloric acid, and boil. If it dissolves, analyse as usual.

(*b*) If it is insoluble in dilute hydrochloric acid, boil with a little strong hydrochloric acid. If soluble, dilute with water, and analyse as usual.

(*c*) If still insoluble, treat the original substance with nitric acid (one part acid to one part water). When nitric acid is used the solution *must* be evaporated nearly to dryness, and the residue taken up with water. On treatment of a metal with nitric acid a white residue may be left. If it dissolves

on adding excess of water it is probably **lead nitrate**, which is insoluble in strong nitric acid. If the residue is insoluble in water it may be **antimony pentoxide**, Sb_2O_5, or **metastannic acid**, $Sn_5O_5(OH)_{10}$.† These oxides will dissolve on boiling with hydrochloric acid.

(*d*) The noble metals, such as **platinum** and **gold**, are only soluble in aqua regia.

Gold and **platinum** may be separated from each other and from most other metals by dissolving in **aqua regia** and evaporating several times to dryness to remove nitric acid. The residue is then dissolved in dilute hydrochloric acid, and the **gold** is thrown out of solution in the metallic form by the action of reducing agents, such as oxalic acid, sulphurous acid, or ferrous sulphate (p. 76). The precipitated gold is filtered off, and the platinum is precipitated as **ammonium platinichloride** (p. 77).

In alloys which contain a large proportion of **silver** or **lead**, gold may be separated by boiling with *nitric acid* in a platinum dish and extracting with water—the residue, after decantation, consisting of metallic gold. When the proportion of gold is high it will protect the alloy from the action of nitric acid. In such cases the alloy may be melted up with an excess of silver or lead, and then treated with nitric acid, when the silver or lead will go into solution and the gold will be left, as already described. The gold being in the form of a fine powder is very often black; the yellow appearance may, however, be made manifest by rubbing or by melting it before the blowpipe.

Cautions.—**1.** Large quantities of substance should not be employed in analysis, because the precipitates produced will be so bulky that difficulty will be experienced in washing

† Metastannic acid, apparently, is not acted on by concentrated hydrochloric acid. It is, however, converted into metastannic chloride, which is insoluble in concentrated hydrochloric acid. If the excess of acid is poured off and water added, it then goes into solution. It may also be dissolved in caustic alkalis.

or dissolving them. Hence the advantages of micro-work (p. 27).

2. Precipitates, unless otherwise stated, **must always** be washed; and the first wash water **must** be added to the solution from which the precipitate has been filtered. If this precaution is omitted the student will in all probability fail to find metals which occur in the barium or sodium group.

3. If the precipitate is to be treated with a solvent, such as ammonium sulphide in the copper group, a small portion of the precipitate should in the first place be subjected to the action of the solvent, because if it is quite insoluble there is no advantage in treating the whole precipitate.

4. If a solution is to be made acid, an excessive quantity of acid must not be employed, as it usually has to be neutralised in a subsequent operation. **A neutral solution is, for this purpose, one which neither turns blue litmus red nor red litmus blue.** A solution is either neutral or it is **not.** When an acid solution is to be made alkaline, the mixture *must be shaken up* and tested with litmus paper after the alkaline solution has been added. Mistakes often occur through the student supposing he has made all his solution alkaline (or acid) when actually the surface of the liquid alone is alkaline (or acid).

5. The use of excessive quantities of "reagents" should be avoided. It is only necessary to employ a sufficient quantity of the reagent to cause the particular reaction to take place, further additions causing an unnecessary increase in bulk, and even at times leading to errors.

6. Should the bulk of solution at any stage of analysis become too great, it must be evaporated to small volume. Instead of this being time lost, it more often results in a saving of time.

7. It is a good rule always to take the same quantity of substance for analysis, say about 0·5 grm. When this is done it is possible with a little experience to judge approximately the relative quantities of the various substances present in the mixture.

General Scheme of Analysis.

To the cold solution add a few drops of dilute **hydrochloric acid**. If a precipitate is produced, continue adding **hydrochloric acid** till no further precipitation takes place, and filter.

- **Residue:** May be AgCl, $PbCl_2$, Hg_2Cl_2. Treat according to scheme on p. 212 (Silver Group).
- **Solution:** If strongly acid, dilute with water or add NH_4OH till it is only slightly acid; *it must not be made alkaline*. Boil and pass H_2S, while still hot, stand, and filter. If **arsenic** has been detected in the preliminary tests, the solution *must* be boiled with sulphurous acid in case the arsenic may be present as an **arsenate.** The boiling must be continued until the solution no longer smells of sulphur dioxide. Excess of hydrogen sulphide is then passed, and the mixture filtered.
  - **Precipitate:** May contain the sulphides of Hg, Pb, Cu, Bi, Cd, Sn, As, Sb, *Au* and *Pt*, or merely sulphur. The washed precipitate is boiled with $(NH_4)_2S$ and filtered.
    - **Residue:** May contain the sulphides of Hg, Pb, Cu, Bi, Cd. Treat by scheme on p. 213 (Copper Group).
    - **Solution:** May contain the thiosalts of As, Sb, Sn, *Au*, *Pt*. Treat according to scheme on p. 216 (Arsenic Group).
  - **Solution:** Boil off H_2S, add 1 to 2 c.c. strong HNO_3, and evaporate to one-half its bulk. Test for **phosphates, organic matter, silica, boric** and **hydrofluoric** acids. In the event of any of these being present, they must be eliminated. While still hot add NH_4Cl and NH_4OH until distinctly alkaline, *i.e.* till the smell of ammonia is permanent. Boil and filter.
    - **Residue:** May be the hydroxides of Fe, Al, Cr, and *Ce*. Examine by scheme on p. 217 (Iron Group I.)
    - **Solution:** Pass hydrogen sulphide until saturated, stand and filter.
      - **Precipitate:** May be the sulphides of Co, Ni, Mn, and Zn. Examine by scheme on p. 218 (Iron Group II.).
      - **Solution:** Boil and add a little ammonia and a slight excess of ammonium carbonate, and filter.
        - **Precipitate:** May contain the carbonates of Ba, Ca, and Sr. Examine by table on p. 220 (Barium Group).
        - **Solution:** May contain the metals Mg, K, Na, and *Li*. Examine by scheme on p. 222 (Sodium Group).

8. All the apparatus employed in chemical analysis must be kept strictly clean. The use of a dirty stirring rod or test-tube may be sufficient to cause the introduction of some foreign substance into the material which is under examination.

9. The micro-tests, especially the drop reactions, are useful as confirmatory tests after the separation has been carried out.

Silver Group.

Add hydrochloric acid to the cold solution until no more precipitate is formed.† Filter and wash the precipitate with a little **cold** water. **Solution :** Examine for the metals of the **copper** and succeeding groups.

The **residue** may be $PbCl_2$, AgCl, Hg_2Cl_2. Boil with water and filter. Residue may be analysed by either of the two following methods (see p. 213).

Precipitation of Sulphur.

The precipitate produced by hydrogen sulphide may be only sulphur, or the precipitate may be mixed with sulphur owing to substances being present which react with hydrogen sulphide. Such substances are **permanganates, chromates, arsenates, nitrites, iodates** (which yield iodine), **bromates, chlorates, ferric salts,** etc. If **permanganates, chromates, arsenates,** or **iodates** are known to be present, the solution should be boiled with **sulphur dioxide** before passing hydrogen sulphide. Care must be taken to remove all the sulphur dioxide, otherwise it will also cause precipitation of sulphur.

† Only a few drops of hydrochloric acid should be added in the first case, because if no precipitate is produced it is not necessary to add more than is sufficient to acidify the solution.

If the solution is alkaline the addition of hydrochloric acid may precipitate gelatinous **silicic acid**; this, however, will only occur if a very large quantity of alkali silicate is present. Feathery crystals of boric acid might be produced from strong solutions of alkali borates, or a heavy white precipitate of **antimony oxychloride** from antimonates or antimonites. Again, if the solution contained the thiosalts of **arsenic, antimony,** or **tin,** the sulphides of these metals would be precipitated.

<table>
<tr><td rowspan="4">**Solution:** Shiny crystals of lead chloride may separate on cooling. Add to the hot solution a solution of **potassium chromate.** A yellow precipitate of lead chromate confirms

Lead</td><td colspan="2">I. **Residue:** Transfer to test-tube; add bromine water, and warm; keep on adding bromine water until the liquid remains a permanent light brown.</td></tr>
<tr><td>**Residue:** Is a mixture of AgCl and AgBr. Dissolve in a little warm strong ammonia. Addition of nitric acid to solution reprecipitates the halogen silver salts, thus confirming
Silver.</td><td>**Solution:** Contains the mercury. Boil off excess of bromine water. Add a few drops of nitric acid and a piece of copper foil. A silver-like deposit on the copper foil confirms

Mercury.†</td></tr>
<tr><td colspan="2">II. **Residue:** Shake up with **ammonium hydroxide,** and filter.</td></tr>
<tr><td>**Solution:** Acidify with nitric acid. A white precipitate shows

Silver.</td><td>**Residue:** Is black; this shows presence of **mercurous mercury.** To confirm, dissolve the black residue in aqua regia, dilute with large excess of water, and add a strip of copper foil. A grey deposit on the foil proves the presence of
Mercury.</td></tr>
</table>

The Copper Group.

Boil ‡ the solution obtained from the silver group,§ and pass **hydrogen sulphide** through it.|| The precipitate may be

† The bromine water oxidises the mercurous salt to a mercuric salt and a mixture of mercuric chloride and bromide is obtained

$$Hg_2Cl_2 + Br_2 = HgCl_2 + HgBr_2$$

‡ If arsenic has been shown to be present by the dry reaction, the solution *must* be boiled with sulphurous acid before passing hydrogen sulphide, because it is only with great difficulty that sulphide of arsenic is precipitated from arsenates.

§ If the solution from the silver group is strongly acid, it *must* be diluted or partially neutralised with ammonium hydroxide before passing hydrogen sulphide. Cadmium sulphide is not precipitated in presence of much hydrochloric acid, also **stannic** and **stannous** sulphides do not come down readily when a large excess of acid is present.

|| It is very important that an excess of hydrogen sulphide should be used, otherwise, of course, precipitation will be incomplete. The gas should

HgS, PbS, Bi_2S_3, CuS (all black), CdS, As_2S_3, SnS_2 (yellow), SnS (brown), Sb_2S_3, Sb_2S_5 (orange). When excess of hydrogen sulphide has been passed, boil † and filter. Examine the **solution** for metals of the **iron** and succeeding groups. Wash the **residue** several times with hot water, then transfer to a

<table>
<tr><td colspan="5">Residue: Wash well with hot water, and boil with a little moderately dilute HNO_3 (1 part conc acid, 3 of water), until no further action takes place. Dilute with water, add about 0·5 c.c. dilute H_2SO_4, and about 2-3 c.c. alcohol. N.B.—If it is certain that no lead is present, H_2SO_4 and alcohol should not be added. Filter.</td></tr>
<tr><td colspan="2">Residue: May be HgS, $PbSO_4$, or, possibly, only sulphur. Boil with ammonium acetate, and filter ($PbSO_4$ is soluble in ammonium acetate.)</td><td colspan="3">Solution: Boil off the alcohol; add excess of NH_4OH, boil, and filter.</td></tr>
<tr><td rowspan="2">Residue: Is HgS, or only S. (The sulphur often has a black appearance.) Dissolve in aqua regia. Boil off the fumes of Cl_2, neutralise with NaOH, and acidify with HCl. Now add a clean strip of copper. A metallic deposit on the copper confirms

Mercury.</td><td rowspan="2">Solution: Add K_2CrO_4. A yellow precipitate of lead chromate indicates

Lead.</td><td rowspan="2">Residue: Is $Bi(OH)_3$. Dissolve off the filter paper with a few drops of HCl, and pour the solution into a large beaker of water to which ammonium chloride has been added. A white precipitate of BiOCl confirms

Bismuth.

Or dissolve in HCl and confirm by § 6, p. 51.</td><td colspan="2">Solution: Divide into two portions.</td></tr>
<tr><td>I.
Add KCN till any blue colour disappears and pass H_2S. A yellow precipitate shows the presence of

Cadmium.

Confirm by film or micro test. Before applying the former moisten the sulphide on the asbestos with concentrated HCl.</td><td>II.
Add acetic acid till the dark blue colour disappears, then add potassium ferrocyanide. A red precipitate confirms

Copper.</td></tr>
</table>

be passed or the solution added until the mixture smells strongly of it, and after allowing the mixture to stand on the water bath and filtering off the precipitate, dilute with water, boil, and pass more gas through the solution, to make certain that precipitation is complete. When tin is present it is always necessary to use a very considerable excess of gas, as both stannic and stannous sulphide only come down slowly.

† If a precipitate appears on boiling **tellurium** is present. (See § 1, p. 81.)

test-tube or small beaker, and boil with yellow **ammonium sulphide,** dilute and filter.† The **solution**: Examine for metals of the **arsenic** group. The **residue**: Examine for the copper group (see p. 214).

Solution: Transfer to test-tube, make just alkaline with ammonia, add 5 grms. of solid oxalic acid, boil until the oxalic acid is dissolved. Pass a rapid stream of H_2S through the hot solution for a few minutes.		**Residue**: Is As_2S_3, or possibly only sulphur. Transfer to test-tube; add 3·4 c.c. of strong nitric acid; boil until the precipitate is dissolved. Make just alkaline with ammonia. Add about 3 grms. of solid NH_4Cl and a piece of magnesium wire or ribbon. Cover mouth of test-tube with a piece of filter paper moistened with $HgCl_2$.§ Allow to stand for 15 minutes. A brown or black stain on the paper proves **Arsenic.**
Precipitate is sulphide of antimony. Confirm by film or micro-test. The white oxide film and characteristic iodide film confirm **Antimony.**	**Solution**: Make just alkaline with ammonium hydroxide, and then just acid with acetic acid; ‡ boil and pass H_2S; again boil, and, if necessary, again pass H_2S. A brownish-yellow precipitate indicates **Tin.** Confirm by dissolving the sulphide in 2-3 c.c. concentrated HCl; add to the solution a small piece of zinc, and boil till both the zinc and the precipitated tin are dissolved; dilute with water, filter, and add to a freshly prepared solution of potassium ferri-cyanide; now add a few drops of ferric chloride; a blue precipitate or coloration confirms tin. See §§ 7, 8, and 9, p. 73.	

† Sufficient ammonium sulphide must be used to dissolve the sulphides of the arsenic group which may be present, therefore it is advisable after filtering to wash the precipitate once with a little warm ammonium sulphide, and to add this washing to the original solution. On the other hand, too large an excess is not advisable, because both copper and mercury sulphides are slightly soluble in a large excess; therefore, to avoid error, the solution should be diluted with water before filtering, as these sulphides are less soluble in dilute ammonium sulphide.

Sodium or **potassium hydroxide** may be used to dissolve the sulphides of the arsenic group if stannous tin is not present. If tin has been found by the dry reactions and it is desired to use this solvent, **bromine** water should be added to the solution in hydrochloric acid until it is just coloured. This oxidises the stannous tin to the stannic condition. The excess of bromine must be boiled off before hydrogen sulphide is passed.

‡ Instead of passing H_2S, ammonium sulphide may be added after the addition of ammonia. On now adding acetic acid, a precipitate of tin sulphide is produced.

§ See p. 60.

Arsenic Group.

The **solution** obtained by boiling the **hydrogen sulphide precipitate** with **ammonium sulphide** may contain the **thiosalts** of As, Sn, Sb. Acidify with dilute HCl; the sulphides are precipitated, mixed with more or less sulphur. Filter, transfer the precipitate to a test-tube,[1] and boil with about 3 or 4 c.c. of concentrated hydrochloric acid for a few minutes. Filter and wash (see p. 215).

[1] It is better, in order to avoid loss of the somewhat volatile chlorides of tin and antimony, to boil the precipitate in a small flask, fitted with a cork through which passes a glass tube about two feet long to act as a condenser.

NOTES TO PAGE 217.

* The addition of nitric acid is to oxidise any ferrous iron to the ferric condition.

† If manganese is present in the mixture a portion of it may be precipitated as hydroxide: hence the importance of rapid filtration. In cases where it is suspected, it is advisable to dissolve the precipitate in hydrochloric acid, and, after boiling, to reprecipitate again with ammonium hydroxide. After filtering proceed as described. The filtrate should be added to the original filtrate. If large quantities of manganese or cobalt are present they may be precipitated as hydroxides; in such a case it is better to employ the method of analysis described on p. 218.

‡ **Titanium** may be separated from the metals of this group by the method described in § 9, p. 114, and then confirmed by the cupferron test (§ 8).

§ Instead of using sodium peroxide the solution may be made strongly alkaline with caustic soda, and hydrogen peroxide or bromine water added. The mixture is then treated as described. The oxidising agent is added to convert the chromic hydrate into soluble sodium chromate, and care must be taken to add sufficient to oxidise the whole of the chromic hydroxide.

‖ If cerium is suspected, divide the hydrochloric acid solution into two portions, test one for iron as described, and to the other portion add 2 or 3 grms. of rochelle salt, boil until dissolved, and add excess of ammonium oxalate: a heavy white precipitate shows the presence of **Cerium.**

¶ Ammonium sulphide may be added instead of passing hydrogen sulphide, but it is better to use the gas, because ammonium sulphide often contains small quantities of ammonium sulphate (from oxidation), which then precipitates small quantities of Ba and Sr, should they be present.

SEPARATION OF THE METALS OF THE IRON GROUP. (For Notes, see p. 216.)

Boil the solution from the copper group until it no longer smells of hydrogen sulphide, then add about 1 c.c. of conc. nitric acid, and boil.* **Now add a few c.c. of a solution of ammonium chloride and a slight excess of ammonium hydroxide, boil and filter at once.†** (Filtrate: see II.)

I. The **precipitate** may consist of $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, $Ce(OH)_3$, $Ti(OH)_3$‡. Wash with hot water and dissolve in a small quantity of dilute hydrochloric acid. Transfer the **cold** solution to a beaker or evaporating basin and add sodium peroxide,§ in small quantities at a time, until the mixture is strongly alkaline; boil until all effervescence ceases, and filter.

Residue: May consist of $Fe(OH)_3$ and $Ce(OH)_4$.‖ Dissolve in a little warm dilute hydrochloric acid, and test for iron with $K_4Fe(CN)_6$. A blue precipitate or coloration confirms
Iron.

Solution: May be Na_3AlO_3 and Na_2CrO_4. Acidify with acetic acid, and divide into two portions.

A. Add lead acetate. Yellow precipitate indicates
Chromium.
Confirm by §§ 2 or 6, p. 90.

B. Add a slight excess of ammonium hydroxide, and boil. A white gelatinous precipitate indicates
Aluminium.
Confirm by § 5, p 88.

II. The **solution** may contain $CoCl_2$, $NiCl_2$, $MnCl_2$, $ZnCl_2$ and also **metals** of the barium and sodium groups. Boil and pass H_2S through the hot solution,¶ until it smells strongly of the gas. Filter off any precipitate which may be formed, and wash with a little hot water containing a few drops of ammonium sulphide. Wash the precipitate off the filter paper into a beaker or porcelain basin with cold 2N. HCl, and stir until no more H_2S is evolved, generally from 3 to 7 minutes, and filter. (N.B.—If the precipitate is not black, Ni and Co are absent, in which case the precipitate may be dissolved with warm dilute HCl.)

Residue: May be CoS and NiS. Test for cobalt by means of the drop reactions or by borax bead; blue bead shows the presence of **cobalt.** If the bead is brown, this proves **nickel.** A trace of cobalt might, however, be present. In any case, if the bead is blue, it is necessary to test for nickel.
Dissolve the precipitate in a little hot HCl to which is added a crystal of $KClO_3$. Evaporate the solution just to dryness, dissolve in about 3 c.c. of water, and add a solution of KCN drop by drop, until the precipitate which is first formed just dissolves; boil and then cool. Now add 2 c.c. of 4N. sodium hydroxide, then bromine water until the solution is slightly brown. Warm; a black precipitate of $Ni(OH)_3$ indicates
Nickel.
Confirm with drop reaction or borax bead. Evaporate solution to dryness, and test for **cobalt** with borax bead, and by § 7, p. 106.

Solution: May contain $MnCl_2$, $ZnCl_2$, and possibly a trace of nickel. Boil until it no longer smells of H_2S. Add an excess of NaOH; boil and filter.

Residue: Is $Mn(OH)_2$ and possibly a trace of $Ni(OH)_2$. Confirm **manganese** by
1. Mix a trace of the precipitate with fusion mixture and a little nitre, fuse in the oxidising flame in a loop of platinum wire—a green melt indicates manganese (see p. 97)
2. See §§ 4 and 5, p. 98.
Manganese.

Solution: Contains Na_2ZnO_2, pass H_2S. A white precipitate indicates
Zinc.
Dissolve in a little HCl and confirm by drop reaction or filter ash test (p. 100).

ALTERNATIVE SEPARATION FOR IRON GROUP WHEN THERE IS AN EXCESS OF COBALT OR MANGANESE PRESENT (For Notes, see p. 219.)

To the hot filtrate from the previous group (after the removal of phosphoric acid, etc.), add NH_4Cl and NH_4OH till distinctly **alkaline**, and, without filtering, pass H_2S. Filter † and wash with hot water, or with cold water containing a little H_2S. The precipitate may contain NiS, CoS, FeS, ZnS, MnS, $Cr(OH)_3$, $Al(OH)_3$, $Ce(OH)_3$. Transfer to a small flask, and add a considerable quantity of **cold** 2N. hydrochloric acid, cork the flask, allow to stand for three or four minutes, with occasional shaking, and filter.

Residue: May be NiS and CoS; wash with hot water, and test for **cobalt** with drop reaction. If no **cobalt** is present, confirm **nickel** by dissolving in a little conc. HCl, to which a small piece of **potassium** chlorate has been added; boil till free from chlorine vapours. **Cool.** Make alkaline with **caustic soda**, add excess of **bromine water**, and warm. A black precipitate of $Ni(OH)_3$ confirms

Nickel.

If **cobalt** and **nickel** are present, dissolve as before in hydrochloric acid and potassium chlorate. Evaporate just to dryness, dissolve in water, and add KCN till the precipitate which first forms just redissolves (an excess of KCN should be avoided). Boil for three or four minutes. **Cool.** Make slightly alkaline with NaOH, add **bromine water** in excess, and warm. Filter off the nickel hydrate, evaporate the solution to dryness, and test the residue by means of the drop reaction or borax bead. A sapphire blue shows

Cobalt.

Solution: May contain $FeCl_3$, $ZnCl_2$, $MnCl_2$, $CrCl_3$, $AlCl_3(CeCl_3)$. Evaporate to half its bulk. **Cool**, and add sodium peroxide till strongly alkaline.‡ Or make strongly alkaline with caustic soda, and add hydrogen peroxide. Boil till effervescence ceases, and filter.

Residue: May be $Fe(OH)_3$, MnO_2, $[Ce(OH)_4]$. Wash with warm water, boil for half a minute with dilute HNO_3, and filter.

- **Residue**: Consists of MnO_2. Confirm by drop reaction or by fusing on platinum wire with fusion mixture. A green mass confirms

  Manganese.

- **Solution**: May contain $Fe(NO_3)_3$, $Ce(NO_3)_4$.§ In absence of cerium add NH_4Cl and excess of NH_4OH. A reddish precipitate of $Fe(OH)_3$ shows ||

  Iron.

  Confirm by dissolving in dilute hydrochloric acid, and adding KCNS

Solution: May contain Na_2CrO_4, Na_3AlO_3, Na_2ZnO_2. Cool, and divide into two portions.

- **I.** A yellow solution indicates chromium. Acidify with acetic acid and add lead acetate solution. A **yellow** precipitate proves

  Chromium.

- **II.** Acidify with dilute HNO_3 **and then make alkaline with** NH_4OH. **Boil, and allow to stand two or three minutes. A white gelatinous precipitate shows presence** of

  Aluminium.

  Confirm by the aluminium reagent (p. 88). Filter off the $Al(OH)_3$, and pass H_2S. A white precipitate indicates

  Zinc.

  Confirm by drop reaction (p. 100).

Iron Group.

Before proceeding to separate the metals of the iron group, **organic matter**, if present, must be removed by evaporating the solution from the **copper and arsenic group** to dryness, and igniting, as described on p. 207.

A **small** portion of the solution must be tested for **phosphoric acid** by boiling off the excess of hydrogen sulphide, making strongly acid with concentrated nitric acid, adding excess of **ammonium molybdate**, and warming to 60° or 70°. (*On no account must the mixture be boiled.*) Should a yellow precipitate be produced, phosphates are present, and must be removed as described on p. 118.

Boric and hydrofluoric acid, if present, should also be removed by evaporating to dryness two or three times with concentrated **hydrochloric acid.**

NOTES TO PAGE 218.

† If the solution has a brown colour, this is owing to too much ammonium hydroxide having been added and to the slight solubility of nickel sulphide in it. Add a little acetic acid to the brown solution, boil, and filter; the nickel sulphide will be thus precipitated, and may be mixed with the rest of the precipitate, or separately tested with dimethyl glyoxime.

‡ The sodium peroxide should be added in small quantities at a time, the amount required depending upon the quantity of the substances in solution. The advantage of using sodium peroxide is that it contains no alumina, while caustic soda sometimes contains considerable quantities, and may thus be a source of error in analysis.

Bromine water is sometimes used as an oxidising agent, but when it is employed, some part of the manganese is often converted into manganate or permanganate, and thus interferes with the detection of the chromium.

§ In order to test for **cerium** in presence of **iron,** the solution is divided into two portions, the smaller of which is tested for iron by diluting with water and adding KCNS. To the second and larger portion is added an excess of citric acid, and it is then made just alkaline with NH_4OH. The citric acid prevents the precipitation of **ferric** and **ceric hydroxides.** Excess of oxalic acid is now added, when a white precipitate of cerium oxalate is obtained.

|| Traces of nickel and cobalt may be found here, since their sulphides are not quite insoluble in dilute hydrochloric acid; they cannot, however, be confounded with iron.

Barium Group.

To the hot solution from the **iron group** add a slight excess of $(NH_4)_2CO_3$, allow to stand five minutes, and filter. (*Cf.* p. 125.) Precipitate may be the carbonates of **barium, strontium,** and **calcium.** Should there be a large quantity of solution from the iron group, it must be evaporated to small bulk before adding $(NH_4)_2CO_3$. Wash the precipitate with hot water. Pierce a hole through the bottom of the filter paper, and wash the precipitate into an evaporating dish with a little dilute HNO_3. Evaporate to dryness. As the nitrates may on no account be ignited, it is best to complete the evaporation on the water bath.

Dissolve a *small* portion of the residue in warm water, cool, and add $CaSO_4$ solution.

(i) An immediate precipitation is produced—**barium** is present.

(ii) A precipitate is slowly formed, barium is absent—**strontium** is present.

(iii) No precipitate produced, barium and strontium are absent—**calcium** may be present. Dissolve the rest of the residue in water, add one or two drops of ammonia and then ammonium oxalate: a white precipitate confirms **calcium.**

If a precipitate was produced with $CaSO_4$, proceed by one of the following methods :—

I. Treat the dry residue with 2 c.c. of strong nitric acid, stir the mixture for a minute or two, and filter through a funnel with a long tube, as described on p. 25.

II. Add 2 to 3 c.c. of a mixture of equal volumes of absolute alcohol and ether to the dry nitrates, and, after stirring, filter (the filter paper should be first moistened with absolute alcohol). Wash the residue twice with small quantities of a mixture of alcohol and ether.

<table>
<tr><td rowspan="2">Solution: May contain $Ca(NO_3)_2$, this salt being soluble in strong nitric acid. Render the solution just alkaline with NH_4OH, and add ammonium oxalate. A white precipitate indicates
Calcium.
Confirm with flame and crystal tests † and spectroscope (pp. 9, 197).</td><td colspan="2">Residue: May contain $Ba(NO_3)_2$ and $Sr(NO_3)_2$, both these nitrates being insoluble in concentrated nitric acid. Wash with a little strong HNO_3 to remove traces of calcium. Then dissolve on the filter with a little hot water. Make just alkaline with ammonium hydroxide, add a slight excess of acetic acid, then K_2CrO_4, ‡ and filter.</td></tr>
<tr><td>Residue: Is barium chromate. Confirm by flame test. The flame is coloured green, and shows the characteristic bands for barium when viewed through the spectroscope. Confirm by rhodizonate test
Barium.</td><td>Solution: Add 2 to 3 drops of concentrated sulphuric acid, and about 3 c.c. of $(NH_4)_2SO_4$. A white precipitate of strontium sulphate indicates
Strontium.
Confirm by flame and rhodizonate tests and by spectroscope.</td></tr>
</table>

<table>
<tr><td colspan="2">Residue: Dissolve the nitrates in a little warm water, add 2 or 3 c.c. of strong HCl, and evaporate to dryness. Stir the residue with a little absolute alcohol and ether. Filter.</td><td rowspan="2">Solution: May contain $Ca(NO_3)_2$. Evaporate to dryness on the water bath, dissolve in a little water and add a few drops of ammonium hydroxide, and then ammonium oxalate. A white precipitate shows
Calcium.
Confirm by flame test and spectroscope.</td></tr>
<tr><td>Solution: Contains $SrCl_2$. Evaporate to dryness, and confirm by rhodizonate or flame test and spectroscope. Dissolve remainder of residue in a very little water and add 2 drops of conc. H_2SO_4 and 3 c.c. $(NH_4)_2SO_4$. Allow to stand. A white precipitate confirms
Strontium.</td><td>Residue: Wash two or three times with a little alcohol. Test by means of flame coloration for barium. Dissolve the remainder of the residue in a little water, and add K_2CrO_4. A yellow precipitate confirms
Barium.</td></tr>
</table>

† The precipitates should always be moistened with strong hydrochloric acid before applying the flame or spectroscope test.

‡ Potassium chromate should only be added to a small portion of the solution. If a precipitate is produced, then it must be added to the whole of the solution. In the event of no precipitate being formed, the bulk of the solution is used to test for **strontium.**

Sodium Group.

Evaporate the solution from the **barium group** to dryness † and ignite gently until no more fumes are given off. Dissolve in a little dilute HCl, and filter from any residue. Divide the solution into two unequal portions.

I. **Smaller Portion.**—(*a*) Add 1 c.c. ammonium chloride, then 2 c.c. Na_2HPO_4 and 3 or 4 c.c. strong NH_4OH. Shake up, and rub the sides of the test-tube with a glass rod; allow to stand a few minutes. A white crystalline precipitate of $Mg(NH_4)PO_4$ shows the presence of **magnesium.**

(*b*) Confirm by the "magneson" reagent (§ 5, p. 136).

II. **Larger Portion,** if magnesium is present.‡ Add a slight excess of $Ba(OH)_2$, boil, and filter. The residue is magnesium hydroxide, and may be discarded. Now pass carbon dioxide gas through the solution,§ boil for a minute or two, and filter. Evaporate the solution to dryness. Test for potassium by means of flame coloration.||

1. The flame is coloured violet—presence of **potassium,** absence of sodium.

† The solution should be evaporated on the sand bath till it begins to spirt. The final evaporation should then be carried out on a water bath, and the ignition should only be commenced when the residue is quite dry. (See p. 138.)

‡ If magnesium is not present, do not treat with $Ba(OH)_2$, but test at once for sodium and potassium.

§ On passing CO_2 through the solution the barium hydroxide is converted into barium carbonate; as, however, part of it will probably be converted into the bicarbonate, it is necessary to boil the solution in order to decompose this. Ammonium carbonate may be used instead of CO_2, but in this case the solution must be evaporated to dryness and ignited to drive off the ammonium salts before hydrogen platinichloride is added.

|| If the presence of **lithium** is suspected, a few drops of hydrochloric acid should be added to the residue before testing for potassium and sodium; the solution must then be evaporated quite to dryness, and the residue extracted with a mixture of equal volumes of ether and absolute alcohol. The solution will contain the lithium chloride, which on evaporating off the solvent may be confirmed by the flame test, or the reactions on p. 133. The residue of sodium and potassium chlorides is dissolved in a little water and treated as described above.

2. The flame is yellow—presence of **sodium**, potassium may also be present. Examine through blue glass, and if the flame has a lilac colour, potassium is also present.

A. Confirm potassium by dissolving a portion of the residue in a very small quantity of water, (*a*) add 1 drop HCl and a small quantity of H_2PtCl_6 and an equal volume of alcohol. Golden-yellow crystals confirm potassium. (*b*) Apply the triple nitrite crystal test (§ 6, p. 129). (*c*) Confirm with $Na_3Co(NO_2)_6$.

B. To another portion dissolved in a little water (*a*) add K_2HSbO_4, a white precipitate confirms sodium. (*b*) Apply the uranyl zinc acetate test (§ 3, p. 131) for sodium.

Systematic Examination for Acids.

By the study of the behaviour of the substance towards solvents, and by the absence or presence of certain metals, an idea of what acids may be present can be formed. Thus, if the substance is soluble in water, and bases of the **barium group** have been found, then **sulphuric, carbonic,** or **phosphoric acids** are not present. Should **silver** be present, and the substance be soluble in water, evidently **chlorides, bromides,** or **iodides** are not present. Similar considerations will indicate whether it is necessary to remove the bases. In all probability, moreover, a fair idea of what acids are present will have been obtained from the preliminary examination.

Note.—The student is cautioned against wildly applying tests for acids which cannot possibly be present. Analysis **must** be systematic, but the students who allow any carefully worked out scientific system to cause them to become mere machines, going through operation after operation without taking the trouble to think whether it is necessary or not, *need never expect to excel, neither will their work be trustworthy*.

Preparation of a Solution in which to Test for Acids (Anions).

I. If the substance is **soluble** in water or dilute acids, and does not contain metals of the copper, arsenic, or iron groups, then the solution may be employed to test for the acids without further preparation.

II. If it is soluble but contains heavy metals, it is advisable to remove them by adding to the solution sufficient sodium carbonate to precipitate the metals as carbonates, which are filtered off, and the solution, after neutralising with acetic acid, tested for the acids,† *e.g.*—

III. If arsenic or antimony is present, it should be removed by acidifying the solution (after it has been treated with sodium carbonate) with acetic acid, and passing hydrogen sulphide. Before testing for the acids, the gas *must* be boiled off.

IV. The substance is **insoluble** in water and acids. In this case fusion or treatment with a large excess of sodium carbonate may be necessary. (See p. 24.) Add to the substance about three times its bulk of solid sodium carbonate and just sufficient water to bring the sodium carbonate into solution. Boil for 5 minutes, filter, and then wash with several small quantities of hot water. The solution may then be tested for acids. If halogen silver salts are present, it is best to add zinc and sulphuric acid, and proceed as directed on p. 207.

In testing for the acids use small quantities of the solution, and always reserve a considerable portion for confirmatory tests.

† It is sometimes difficult to remove copper by simply boiling with sodium carbonate. If the solution after boiling with sodium carbonate is blue, acidify with acetic, and pass hydrogen sulphide.

$$5ZnSO_4 + 5Na_2CO_3 + 3H_2O = 2ZnCO_3, 3Zn(OH)_2 + 5Na_2SO_4 + 3CO_2$$

If **arsenic** or **chromium** has been found when analysing for the metals, ascertain, by taking a small portion of the original mixture, whether they were there as **anions** or **cations**, and then remove them before testing for the other acids.

Preparation of a Neutral Solution.—The best way to prepare a neutral solution is, if the solution is alkaline, to make it slightly acid with acetic acid, then add a slight excess of ammonia, and boil until the excess of ammonia is driven off. If it is originally acid, add a slight excess of ammonia and proceed as above. For acid groups, see p. 227.

As already stated (p. 140) the majority of the acids may be divided into five groups, according to their behaviour with **silver nitrate** and with **barium chloride**. For convenience of reference the groups are reproduced here:—

Group I.—HCl, HBr, HI, HCN, $H_4Fe(CN)_6$, $H_3Fe(CN)_6$, $HClO$, $HCNS$.

Group II.—H_2S, H_3PO_2, H_2SO_3, $H_2S_2O_8$, HNO_2.

Group III.—H_3PO_4, HPO_3, H_3PO_3, $H_4P_2O_7$, $H_2S_2O_3$, H_3BO_3 (in strong solution), H_3AsO_3, H_3AsO_4, H_2CrO_4, H_2SiO_3, HIO_3, H_2CO_3.

Group IV.—H_2SO_4, HF.

Group V.—HNO_3, $HClO_3$, $HClO_4$, $HMnO_4$.

NOTES TO ACID TABLE I. (See next page.)

† If a precipitate is produced which is soluble in hot water, it points to the presence of **nitrites**, **sulphates**, or **borates**, the silver salts of which are only precipitated from fairly concentrated solutions, and are soluble on boiling.

‡ Even if the precipitate is reduced on boiling, the whole of it should be treated with nitric acid.

§ It must be remembered that silver nitrate gives a brown precipitate with ammonia, but with a little care and experience there is very little chance of mistaking this brown colour for that of the acids mentioned. If arsenic and chromium have been removed, as recommended, from the original solution, arsenates, arsenites, or chromates will not be found here.

|| If cyanides are not present, the silver nitrate is added to a portion of the original solution, acidified with nitric acid.

ACID TABLE I. (For Notes, see p. 225.)

To a portion of the solution prepared for the acid tests, which has been rendered **neutral**, add a slight excess of **silver nitrate.**

<table>
<tr>
<td rowspan="2">No precipitate is produced: absence of Groups I., II., and III.</td>
<td colspan="2">A precipitate is formed—presence of Group I., II., or III. Boil the mixture; if the precipitate dissolves, see note.† After boiling, if the precipitate does not dissolve, decant off excess of solution, and warm with a few c.c. of dilute nitric acid; ‡ filter if necessary.</td>
<td>If reduced on boiling ↓</td>
</tr>
<tr>
<td>Solution: May contain acids of Groups II. and III. Pour a few drops of the solution into a watch-glass, place the glass upon a piece of white paper, and by means of a glass rod let a drop of ammonia fall into the middle of the solution. A coloured ring is produced,§
Yellow→H_3AsO_3, H_3PO_4
Brown→H_3AsO_4
Brick red→ H_2CrO_4
White→H_2SO_3, HPO_3, $H_4P_2O_7$</td>
<td>Residue consists of one or more of the acids of Group I. If it is readily soluble in dilute ammonia, then it is AgCl or AgCN. If it is light yellow, HI is present; if orange-yellow, $H_3Fe(CN)_6$. In the latter case test a portion of the original solution for ferricyanides and ferrocyanides, p. 153. Test for HCN by placing a few drops of the original neutral or alkaline solution in an evaporating basin with a few drops of yellow ammonium sulphide, and evaporate to dryness on a water bath. Take up with a few drops of dilute hydrochloric acid, and add a drop of $FeCl_3$, a red coloration shows the presence of cyanides (p. 151). If a cyanide is present, acidify a portion of the original solution with dilute nitric acid, and boil until HCN is no longer given off. This solution contains the halogen acids (if present). Add silver nitrate ‖ to a portion of the solution. If a precipitate is produced, which is readily soluble in dilute ammonia, then HI is not present—HBr probably not. But test for HBr by taking a fresh portion of the solution, add a few c.c. of carbon disulphide, a little calcium hypochlorite solution, and then a drop of acetic acid. If on shaking up the carbon disulphide becomes coloured brown, then HBr is present.
If the silver salt is insoluble in strong ammonia, then HI is present. In case HI is present, test for HBr in original solution by § a, p. 147. HI may be confirmed by § 6, p. 146. In presence of the other halogens HCl must be tested for by § 5, p. 143.</td>
<td>The precipitate becomes brown or black on boiling; some acid or acids of Group II., the silver salts of which are reduced on boiling, are present. Test for these separately in small quantities of the original solution:
H_3PO_2, § 1, p. 179.
H_2SO_3, p. 167.
If the precipitate was black or brown as soon as produced, then H_2S or $H_2S_2O_3$ is present. Test separately for H_2S, § 3, p. 170, and for $H_2S_2O_3$, § 4, p. 167.
NOTE.—All these acids should have been indicated in the preliminary reactions.</td>
</tr>
</table>

ACID TABLE II.

To a portion of the original hot **neutral** solution, add an excess of **barium chloride.**

<table>
<tr><td rowspan="2">No precipitate is produced : absence of Groups III. and IV.</td><td colspan="2">A precipitate is formed. Treat with a little dilute hydrochloric acid, and warm.</td></tr>
<tr><td>The precipitate dissolves : absence of Group IV., HF and H_2SO_4.</td><td>Precipitate does not dissolve. Group IV. is present. HF, if present, will have been found in the preliminary reactions. Boil the precipitate with an excess of strong HCl ; if it is still insoluble, then sulphuric acid is present.†</td></tr>
</table>

Observe.

Group I.—**Hypochlorites** will have been indicated in the preliminary tests : confirm by § 4, p. 150.

Group II.—**Persulphates** : confirm by §§ 3 and 4, p. 167.

Sulphites.—Test for sulphites by adding a few c.c. of bromine water. A white precipitate confirms H_2SO_3.

Group III. is present : all these acids should have been found in the preliminary tests or when testing for the metals.

Other Tests.

I. Add **ferric chloride** to solution acidified with hydrochloric acid.

1. Blood-red coloration disappearing on addition of mercuric chloride : **thiocyanic acid.**

2. Olive-brown : hydroferricyanic acid.

3. Deep blue precipitate, turning brown on addition of excess of caustic alkali : **hydroferrocyanic acid.**

For separation of ferro- and ferricyanides, see p. 156.

4. Iodine may be liberated from iodides ; it dissolves in carbon disulphide, forming a violet solution.

II. On adding **ferric chloride** to a neutral solution, beside the above colorations the following will also be shown :—

† CaF_2 is soluble in hot strong HCl.

1. **Red coloration,** which disappears on boiling, a brown basic iron salt being precipitated: **sulphurous acid, acetic acid, formic acid.**

2. **Reddish-violet coloration,** colour vanishes on warming: **thiosulphuric acid.**

Borates may be tested for by taking a small portion of the original mixture and treating it according to § 3, p. 181.

Thiosulphates: on warming a little of the original solution with dilute sulphuric acid, sulphur is precipitated, sulphur dioxide evolved.

Phosphates should have been tested for after removing the metals of the copper and arsenic groups.

Silicates will either have been found in preparing a solution of the substance, or before testing for the metals of the iron group, or in the borax bead.

Iodic Acid: confirm by § 7, p. 146.

Group IV.—**Nitrites** will have been indicated in the preliminary tests: confirm by §§ 2 and 7, p. 164.

Chlorates and **Perchlorates** will have been found in the preliminary examination on warming with strong sulphuric acid.

Nitrates.—Test a portion of the original solution by the brown ring test (§ 3, p. 162). If **nitrites, bromides,** or **iodides** are present, test for **nitric acid** by the brucine and nitron tests (pp. 162, 163).

The presence of **permanganate** will have been recognised by the intense violet-red colour of the solution, the colour disappearing when the solution is warmed with dilute sulphuric and oxalic acids.

Hydroxyl Ion in presence of soluble **carbonates.** To the solution add an *excess* of barium chloride. This precipitates the CO_3'' as barium carbonate. On now adding phenolphthalein a red coloration is produced if OH' is present. The barium chloride is added in excess in order to prevent the $BaCO_3$ from being ionised.

Organic Acids.

If the substance chars when heated in a dry tube, organic acids must be looked for.

For the analysis of organic acids, see Part II. In the grouping as above set out, certain organic acids might be found, *e.g.* **tartaric acid, oxalic acid,** in Group III.

PART II.

ORGANIC ANALYSIS.

CHAPTER XI.

QUALITATIVE "ELEMENTARY" ANALYSIS OF CARBON COMPOUNDS.

Detection of Carbon.—1. Most organic substances char when strongly heated, with evolution of combustible gases.

2. When heated with concentrated sulphuric acid, many organic compounds blacken, owing to separation of carbon.

3. Some substances answer to neither of the above tests; in this case the substance is dried at 100°, finely powdered, mixed with seven or eight times its bulk of powdered dry **copper oxide**, and heated gently at first (so as not to lose any of the carbon compound before it has reacted), and then strongly. A glass rod which has been dipped in lime water is held in the mouth of the tube, or the gases evolved are bubbled through lime water. If the latter is rendered turbid, the presence of carbon is proved. All organic substances, with the exception of some cyanides, yield carbon dioxide when treated in this manner.

Detection of Hydrogen.—Heat the substance as above with dry **copper oxide**. If hydrogen is present in the compound it will be converted into water, which will, as a rule, condense on the cool portions of the tube. If, however, the quantity of water produced is very small, its presence can be made apparent by dusting the upper portions of the tube with a little white **anhydrous copper sulphate**, which will be turned blue by the water.

Detection of Nitrogen.—1. Many organic compounds which contain **nitrogen** evolve ammonia when strongly heated in

a hard glass test-tube with soda lime. As, however, all organic compounds which contain nitrogen do not yield it up as ammonia, the following is a better method.

2. Heat a small portion of the substance in a test-tube, with a small piece of metallic **sodium** or **potassium**—first gently, finally to redness; dip the hot end of the test-tube into a small basin containing a little water: † the tube will break, and the contents become mixed with water. Filter off from the carbonaceous residue; add a small quantity of a solution of **ferrous sulphate**; boil and acidify with hydrochloric acid; if nitrogen be present, a blue precipitate or merely a bluish-green coloration will be produced. The reaction which takes place is as follows: The sodium combines with the nitrogen, forming **sodium cyanide**; and, since the solution is alkaline from the action of the excess of sodium on the water, when ferrous sulphate is added ferrous hydroxide is produced, which, when warmed with the sodium cyanide, is converted into **sodium ferrocyanide.**

$$Fe(OH)_2 + 6NaCN = Na_4Fe(CN)_6 + 2NaOH$$

On acidifying the mixture, the ferric chloride which is produced in the solution owing to oxidation of the ferrous salt, acts upon the sodium ferrocyanide, with formation of "Prussian blue."

$$3Na_4Fe(CN)_6 + 4FeCl_3 = Fe_4[Fe(CN)_6]_3 + 12NaCl$$

Sometimes the addition of a ferric salt is recommended, but usually sufficient is formed during the reaction.

Detection of Chlorine, Bromine, and Iodine.—1. Heat a piece of copper wire in the flame of the Bunsen burner until it is black, and ceases to colour the flame green. Now dip the hot end of the wire in the substance to be tested

† The operation of dipping the hot test-tube in water must be done with caution, because it often happens that some of the sodium has not been oxidised, and therefore, when it comes in contact with water, may cause a slight explosion.

(whether liquid or solid), and again introduce into the Bunsen flame. If a **halogen** is present a green or blue coloration is produced. This test is not always certain; further, it gives no information as to which of the halogens is present.

2. Mix a little of the substance to be tested with two or three times its bulk of **sodium carbonate,** and about its own bulk of **potassium nitrate** or **sodium peroxide,** and fuse in a crucible or on a piece of platinum foil. Dissolve in water; acidify with nitric acid, and apply the usual tests for the halogens.

3. The best method is as follows: Heat a little of the substance with **sodium,** as already described in testing for nitrogen. If halogens are present, their sodium salts are produced; and, on filtering the solution obtained after breaking the test-tube in water, and acidifying with nitric acid, the usual tests for the halogens may be applied.

Detection of Sulphur.—**1.** Fuse a little of the substance with **sodium carbonate** and **potassium nitrate** or **sodium peroxide** as described above, in § 2, for the halogens. Test the solution obtained, after dissolving in water and acidifying with hydrochloric acid, for a **sulphate** by means of barium chloride.

2. Ignite the substance with **sodium,** dissolve in a little water, filter, and place a drop or two of the solution on a watch-glass, and add a drop of a solution of **sodium nitroprusside**; if sulphur is present, a brilliant violet coloration will be produced, the sulphur having combined with the sodium to form sodium sulphide. The sulphide may also be tested for by acidifying with acetic acid, and adding a drop or two of a solution of a lead or silver salt, when a black precipitate will be produced.

Sulphur and Nitrogen.—If sulphur and nitrogen occur together, sodium thiocyanate will be produced when the organic substance is ignited with sodium. Acidify a portion of the solution obtained after ignition with sodium, with hydrochloric acid, and add ferric chloride. A blood-red coloration

indicates the presence of sulphur and nitrogen in the original substance.†

Detection of Phosphorus.—1. Fuse with **sodium carbonate** and **sodium peroxide** or **potassium nitrate.** Dissolve the fused mass in water, make strongly acid with concentrated nitric acid, add **ammonium molybdate,** and warm : a yellow precipitate indicates the presence of phosphorus.

N.B.—When the substance to be tested is a liquid, saturate some fibres of recently-ignited asbestos with it, and apply the tests as above. Liquids can, unless very volatile, be ignited directly with sodium.

Determination of Boiling- and Melting-Points.

As a test of the purity of an organic substance, the determination of the boiling- or melting-point is of great value. If a pure liquid is distilled, the boiling-point will remain constant from the beginning of the operation until the whole of the liquid has been distilled. If, on the other hand, the liquid is a mixture of two or more substances whose boiling-points lie some distance apart, then various fractions may be collected, each one of which will have a different boiling-point. For boiling-point of small quantities, see p. 242.

A solid substance will usually melt *sharply* the moment the temperature at which it fuses is reached. If it be impure it will generally appear to shrink and soften before the correct melting-point is arrived at, and there may be a considerable number of degrees between the point at which it commences to melt and that at which it has all actually become fluid. The determination of the melting-point is, therefore, an

† The tests for the halogens, nitrogen, and sulphur may be all carried out with one portion of the substance. It is ignited with sodium, and, after addition of water and filtration, the solution is divided into four portions, which are separately tested.

important test of purity, and it is also of great value in identifying a compound.

Determination of Boiling-Point.—The determination may be carried out in a fractionating flask, A (Fig. 20), which should be connected with a condenser, B. The neck of the flask is closed with a cork, through which passes a thermometer, *t*, the bulb being placed immediately below the outlet tube, C.

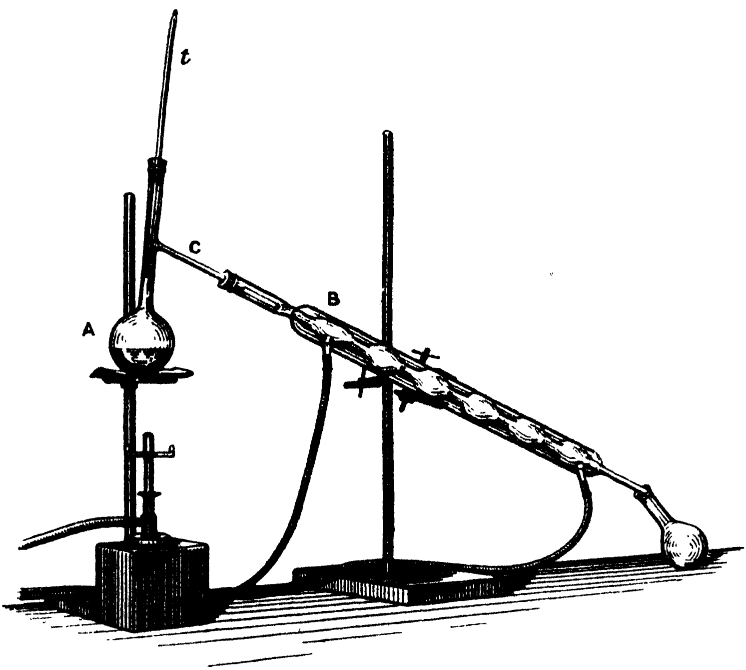


FIG. 20.

A few pieces of broken glass or porcelain are put in the flask to prevent "bumping" or sudden boiling. In the case of liquids which boil at a temperature above 125° C., a glass tube without a water jacket is used instead of a Liebig's condenser, which is liable to crack. To determine the boiling-point, the liquid is placed in the fractionating flask, which should be about one-third full. It is then heated, and as

soon as it begins to distil the temperature is noted. If, after about one-third of the liquid has been distilled, the temperature is still the same, the liquid may be said to be pure. If the temperature is not constant, it is obvious that a mixture of substances is being dealt with. When the quantity of substance is very small, the determination of the boiling-point may be carried out by the micro-method described on p. 242.

Separation of Liquids by Fractionation.—When the boiling-points of two liquids are a long interval apart, it is often an easy matter to separate the liquids by fractionation, as just described. The liquid of the lower boiling-point distils over first, and, as soon as it has all passed over, the boiling-point rapidly runs up and becomes constant again some degrees higher. When, however, the boiling-points are fairly close together, it is necessary, in order to get a separation, to employ a fractionating column. Fig. 21 represents such a column, "Young's Column," which consists of a series of pear-shaped bulbs.

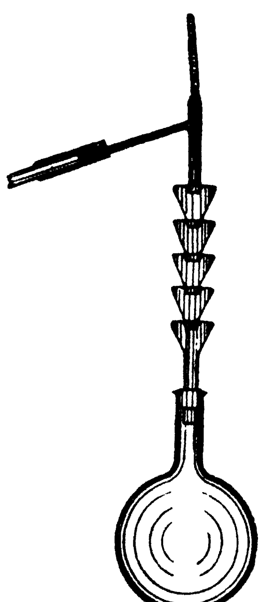


FIG. 21.

Exercises in Fractional Distillation.—1. Make a mixture of 30 grms. acetone and 15 grms. aniline, and distil in the apparatus illustrated in Fig. 20. With care a complete separation should be obtained.

2. Another good exercise is to fractionate commercial benzene. Use apparatus shown in Fig. 21.

Steam Distillation.—Many substances, which can only be distilled with difficulty, are found to be much more volatile

when distilled in a current of steam. Again, some substances, which under ordinary circumstances are decomposed when subjected to distillation, may be readily distilled with the aid of steam. Steam distillation is also of great use in distilling a mixture containing a volatile and a non-volatile substance, one or other of which might be decomposed by heating in the ordinary way. For example, a mixture of aniline and sugar or of nicotine and cinchonine; the aniline or nicotine will pass over with the steam, but the sugar and cinchonine will remain behind. In the course of this book the student will on several occasions be recommended to employ distillation

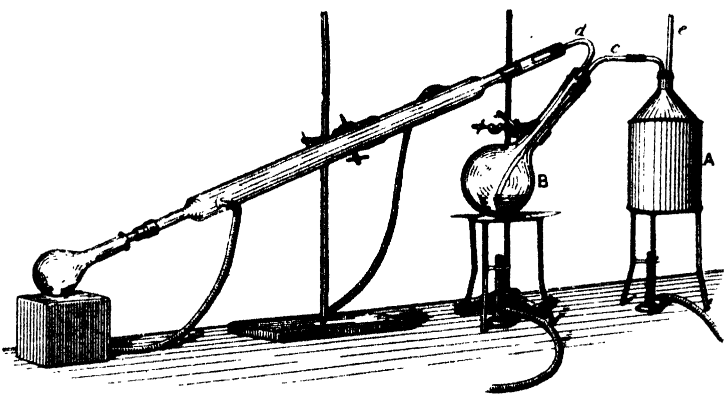


FIG. 22.

by steam as a method of separation, therefore it has been thought advisable to describe the apparatus which is generally used.

The apparatus (Fig. 22) consists of a tin or, better, copper can, A, which is half full of water, and is connected by means of a rubber tube to a glass tube, *c*, which passes nearly to the bottom of a round-bottomed flask, B. The flask, B, contains the liquid which it is desired to distil, and is connected, by means of the tube *d*, with a Liebig's condenser. The long, open upright tube, *e*, in the tin can is a safety tube; it passes to within about 1 inch of the bottom of the can, so that should the water be below this level, steam will issue from the top of

the tube; or should the pressure in the flask become too great, it will act as a safety valve.

Determination of Melting-Point.—The apparatus employed for determining the melting-point (Fig. 23)consists of a beaker, A, of about 40 to 60 c.c. capacity, containing sulphuric acid or glycerol, or, for substances with a low melting-point, water, and fitted with a circular glass stirrer, B. A very small quantity of the substance is placed in a capillary tube, C,

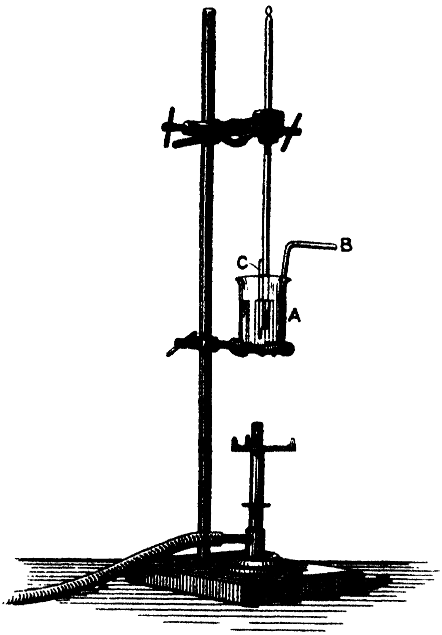


FIG. 23.



FIG. 24.

closed at one end, which is bound to the thermometer bulb by means of a thin rubber band round the portion out of the liquid. The acid is cautiously heated, being constantly stirred, and the temperature at which the substance becomes liquid is noted. This is its melting-point (m.p.).

Extraction with Ether.—The cold solution to be extracted is transferred to a separating funnel (Fig. 24). A layer of

ether about 1 cm. deep is poured on to the solution, the stopper is replaced and the liquids mixed by combined rotation and inversion, so that the ether may thoroughly mix with the aqueous solution. One finger should be placed over the stopper while shaking, otherwise the pressure exerted by the volatile ether may cause it to fly out. As soon as the ethereal layer has completely separated, the lower aqueous layer is run off by opening the tap of the funnel. The operation should be repeated with another small quantity of ether. The extraction is always more complete when successive small quantities of ether are employed, than by adding a large quantity of ether at one time. Vigorous shaking should be avoided, as in some cases emulsions form which will not readily separate into two layers.

In order to test the substance which has been extracted, the ethereal solution is transferred to a distillation flask and the ether is distilled off. When chloroform is used as a solvent it forms the lower layer in the funnel, being heavier than water.

As an exercise take 2 grms. of aniline, mix it with 50 c.c. of water, and extract with ether. After separation dry the ethereal extract with a few small pieces of anhydrous calcium chloride. After standing for 15 minutes decant from the calcium chloride into a weighed flask, washing the calcium chloride with 5 c.c. of ether, and distil off the ether on a water bath. The resulting aniline should weigh 2 grms.

Organic Micro-Analysis.

Many analytical operations such as dissolution, filtration etc., are common to both inorganic and organic materials, and for these reference should be made to the Inorganic section (p. 27), where the advantages and limitations of micro-methods in general are also discussed. The present chapter, deals only with those micro-methods which have special application to organic compounds. The student should also study the "Handbook of Chemical Microscopy," by Chamot and Mason.

Melting-Points.—The usual melting-point tubes require very little material, but if only a single crystal is available it may be placed on the flat surface of a glass trough through which water or another liquid at a known temperature flows (Fig. 25); the crystal should be immediately over the bulb of the thermometer. The temperature is gradually raised, and the melting-point is observed by means of a lens.

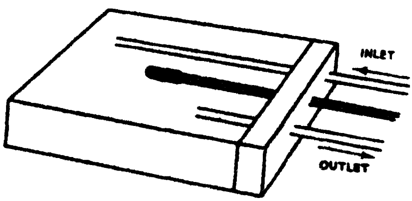


FIG. 25.

For higher temperatures crystals of two substances of known melting-points should be heated on a hot plate by the side of the sample, a choice being made such that one melts at a temperature just above the melting-point of the sample, and the other just below it; the melting-point of the sample is then between two known values.

Boiling-Points.—It is often necessary to determine the boiling-point of very small quantities of liquids. The apparatus employed for this purpose is illustrated in Fig. 26.

A flask which holds about 100 to 110 c.c. of fluid is placed upon a wire gauze fastened over an inverted cone, such as is used to prevent Bunsen burners from flickering. The flask has a very wide neck, about 4 cm. in diameter, and is fitted with a cork with three holes. Through the central hole a thermometer is passed, and through A a small thin-walled test-tube, about 7 to 8 cm. long, with a diameter of 0·5 cm. This tube, however, is not passed directly through the cork, but through a piece of glass tube which is fitted into the cork so that the test-tube may be inserted and withdrawn without any difficulty. It also serves to prevent charring of the cork

with sulphuric acid when the test-tube is withdrawn. In order to prevent the test-tube from slipping through into the flask, the top of it is slightly widened out, so as to act as a collar. The thermometer also passes through a similar tube, and to prevent it dropping down too low a piece of rubber tube is placed round it to act as a support. The circular stirrer, B, is made of glass rod and fits loosely through another tube, so that the air, when it expands on heating, shall not set up a pressure.

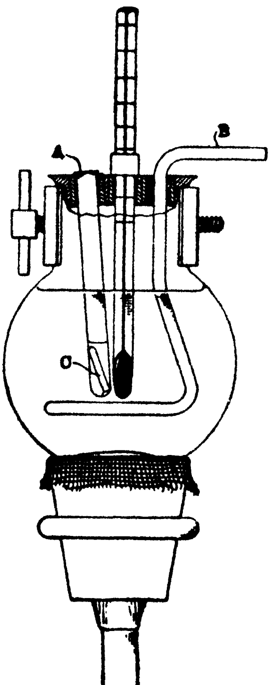


FIG. 26.

About 0·5 c.c. of liquid, the boiling-point of which is to be determined, is placed in the tube, and then a capillary tube, C, sealed at one end, and about 1 to 1·5 cm. long, is dropped into the liquid in such a way that the open end is at the bottom. The determination is then carried out as follows :—

The acid is heated by means of a Bunsen burner, the liquid being gently stirred. The temperature is raised fairly quickly at first until a continuous stream of bubbles is given off from the bottom of the capillary tube. The source of heat is then removed and the temperature allowed to drop, the heating liquid being thoroughly stirred while it cools. As the temperature drops the bubbles begin to be given off less rapidly, and finally stop altogether. At the moment the bubbles cease to be given off—that is, when the pressure of the vapour within the tube is equal to the atmospheric pressure—the thermometer is read, and this is the boiling-point of the liquid. A second determination can be made by at once again rapidly raising the temperature before

the liquid is sucked back into the capillary tube. The stream of bubbles is again obtained, and on cooling down a second reading may be taken as before. It is found that by proceeding in this manner, and being careful to stir, very accurate results may be obtained.

Refractive Index.—A solid is placed on a microscope slide and a drop of a liquid of known refractive index is placed over it, and a cover-slip over the whole. Dark contour lines are seen under the microscope if the refractive indices differ, and other liquids should be tested until one is obtained in which they are at a minimum or invisible. Liquids are tested in a similar way using solids of known refractive index. Some suitable standards are given by Chamot and Mason.

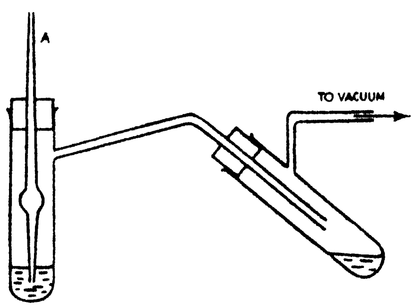


FIG. 27.

Specific Gravity.—The principle used is similar to that indicated for the refractive index, liquids of known specific gravity being chosen so that the solid under examination neither sinks nor floats in it. Liquids are tested with known solids.

Distillation is conveniently carried out by means of the apparatus shown in Fig. 27 which provides for vacuum distillation. This is easily made from small test-tubes, the tube, A, being an inlet tube with a capillary opening at both ends to ensure uniform boiling. For steam distillation it is replaced by a connection leading to another tube containing

boiling distilled water. Both this and the distillation-tube may conveniently be immersed in a glycerin bath.

Sedimentation of solids from large volumes of liquids is achieved by completely filling a Winchester quart bottle with the liquid and inverting it so that the mouth is below the surface of some water contained in a basin. This will support the column of liquid in the bottle, and the solid will gradually accumulate in the basin and can be separated further by means of a micro-centrifuge.

CHAPTER XII.

REACTIONS AND SEPARATION OF ORGANIC ACIDS AND PHENOLS.

THIS chapter is mainly devoted to the reactions of the acids, but, for convenience, the reactions of **phenol** have been placed after those of salicylic acid, and those of **pyrogallol** after tannic acid.

Organic acids all contain the monovalent carboxyl group, COOH, the hydrogen atom of which is replaceable by metals. They are, as a rule, only moderately ionised in solution, and cannot, therefore, be classed among the strong acids. In solution they are ionised into the cation H and the anion R . COO′, where R stands for any complex radical. For example, the ions of acetic acid (p. 249) are H˙ and CH_3COO', whereas those of oxalic acid (p. 253) are 2H˙ and $\begin{bmatrix} COO \\ | \\ COO \end{bmatrix}''$

It is thus seen that the valency of the acid is determined by the number of —COOH groups which it contains. Almost all organic acids form soluble sodium and potassium salts, and are therefore soluble in solutions of sodium and potassium carbonates. **Carbolic acid** (phenol) and **pyrogallic acid** (pyrogallol), etc., are not acids, but are phenols; owing, however, to the negative character of the phenyl group, C_6H_5—, they have an acid character, and dissolve in caustic alkalis to form alkali salts. In pyrogallol the acidic character is so strongly marked that it dissolves even in alkali carbonates. The addition of negative groups to phenol also increases its acidic character, thus **picric acid** (trinitrophenol) forms salts with alkali carbonates and with ammonia. Even nitro-phenols

in which there is only one nitro-group present are able to decompose alkali carbonates.

Organic acids may occur either free, as salts of the alkali metals, as salts of metals other than these, or mixed with various inorganic metallic salts. The usual tests may be applied at once to salts of the alkali metals, and, after neutralisation by sodium carbonate, to the free acids. In all other cases, however, the metals must be removed before the tests for the acids are applied, usually by boiling with a strong solution of sodium carbonate, as recommended in testing for inorganic acids (Part I., p. 224); but certain metallic combinations are not decomposed under these conditions, *e.g.* antimony in tartar emetic. In such circumstances it is necessary to acidify with dilute hydrochloric acid, and to pass hydrogen sulphide. The sulphides are then filtered off, the solution made alkaline with ammonia, and hydrogen sulphide again passed; any further precipitate formed being again filtered off. This procedure will remove all the metals with the exception of those of the alkaline earths, which must be removed by boiling with sodium carbonate. Substances which do not form soluble salts with sodium carbonate, such as aniline, phenol, etc., should be extracted by means of ether before proceeding to analysis. The solution which has been treated by one or both of these methods should now be slightly acidified with dilute hydrochloric acid, and boiled for a few minutes to decompose any alkali sulphides which may have been formed. **In all cases a neutral solution must be prepared before proceeding to analysis.** If, during the above operations, the bulk of solution has become at all considerable, it should be concentrated before applying the tests.

Formic Acid.

H . COOH

Formic acid is a colourless liquid, with a pungent odour. When dropped upon the skin it causes painful blisters. It

freezes to a transparent ice-like solid, which melts at 8·5°; the liquid boils at 100·6.° It is soluble in water in all proportions. Its metallic salts, with the exception of those of **lead** and **mercury,** are also readily soluble in water; the two latter are only slightly soluble.

1. When formates are heated with **soda lime** hydrogen gas is evolved.

$$H.COONa + NaOH = Na_2CO_3 + H_2$$

***2.** Cold concentrated **sulphuric acid,** when added to a formate or formic acid, liberates **carbon monoxide,** which burns with a blue flame on ignition. (Distinction from oxalic acid, which on heating, *not in the cold*, with concentrated sulphuric acid, evolves both carbon monoxide and dioxide, and the evolved gases therefore turn lime water milky.)

$$2H.COONa + H_2SO_4 = 2CO + Na_2SO_4 + 2H_2O$$

3. Dilute **sulphuric acid** liberates formic acid, the presence of which is noticed on warming by its pungent acid odour.

$$2H.COONa + H_2SO_4 = 2H.COOH + Na_2SO_4$$

***4.** When formic acid or a formate is warmed with a little concentrated **sulphuric acid** and **ethyl alcohol,** the pleasant characteristic odour of **ethyl formate** is noticed.

$$2H.COOK + H_2SO_4 = 2H.COOH + K_2SO_4$$
$$H.COOH + C_2H_5OH = H.COOC_2H_5 + H_2O$$

In this and similar reactions sulphuric acid first liberates the acid, and then the excess of the sulphuric acid acts as a dehydrating agent.

***5. Silver nitrate** is reduced when added to a **dilute** solution of formic acid or a formate, the reduction taking place slowly in the cold, rapidly on heating; a black precipitate of metallic silver being obtained.

(*a*) $H.COOK + AgNO_3 = H.COOAg + KNO_3$

(*b*) $2H.COOAg = H.COOH + 2Ag + CO_2$

Ammoniacal solutions of silver salts are **not** reduced, even on warming.

*6. **Mercuric chloride** gives, on warming either with formic acid or a formate, a white precipitate of **mercurous chloride** (distinction from acetic acid). If excess of formic acid or a formate is present, the mercurous chloride becomes reduced to metallic mercury.

(*a*) $2H.COONa + 2HgCl_2 = Hg_2Cl_2 + CO + CO_2 + H_2O + 2NaCl$
(*b*) $Hg_2Cl_2 + 2H.COONa = 2Hg + CO_2 + CO + H_2O + 2NaCl$

*7. **Ferric chloride** produces a red coloration, which is destroyed on addition of hydrochloric acid. When the red solution is boiled a brown precipitate of a basic iron salt is produced.

(*a*) $3H.COONa + FeCl_3 = (H.COO)_3Fe + 3NaCl$
(*b*) $(H.COO)_3Fe + 2H_2O = (H.COO)Fe(OH)_2 + 2H.COOH$

*8. On acidifying a solution of formic acid or a formate with a little dilute sulphuric acid, shaking up with a small quantity of **mercuric oxide**, and afterwards filtering, a solution of **mercuric formate** is obtained.

$$2H.COOH + HgO = (H.COO)_2Hg + H_2O$$

When this solution is boiled a white precipitate of mercurous formate is produced, which rapidly changes to a grey deposit of metallic mercury (distinction from acetic acid).

(*a*) $2(H.COO)_2Hg = (H.COO)_2Hg_2 + H.COOH + CO_2$
(*b*) $(H.COO)_2Hg_2 = 2Hg + H.COOH + CO_2$

Acetic Acid.

$$CH_3.COOH$$

Acetic acid is a colourless pungent-smelling liquid, crystallising to an ice-like solid at 16·5°, and boiling at 118°; the boiling acid is inflammable, burning with a slightly bluish flame. It is readily soluble in water, alcohol, or ether. The

acetates, with the exception of mercurous and silver acetates and a few basic acetates, are soluble in water.

1. Dry acetates, when strongly ignited in a tube, give off inflammable vapours, consisting of acetone and other products.

2. When acetates are heated with either concentrated or dilute **sulphuric acid,** the characteristic "vinegar" smell of acetic acid is noticed. (*Cf.* § 2, p. 248.)

$$2CH_3 . COOK + H_2SO_4 = 2CH_3COOH + K_2SO_4$$

***3.** Acetates or acetic acid, when heated with concentrated **sulphuric acid** and **alcohol,** produce the pleasant and characteristic odour of **ethyl acetate.**

$$CH_3COOH + C_2H_5OH = CH_3COOC_2H_5 + H_2O$$

***4. Silver nitrate,** when added to a strong neutral solution of an acetate, produces a white crystalline precipitate of **silver acetate,** which is not reduced on boiling. (*Cf.* Formates, § 5, p. 248.)

$$CH_3COOK + AgNO_3 = CH_3COOAg + KNO_3$$

***5. Ferric chloride** gives in neutral solutions a deep red coloration, which is destroyed on addition of hydrochloric acid. On boiling the red solution, a brown precipitate of basic **ferric acetate** is produced.

(*a*) $3CH_3COONa + FeCl_3 = (CH_3COO)_3Fe + 3NaCl$

(*b*) $(CH_3COO)_3Fe + 2H_2O$

$$= (CH_3 . COO)Fe(OH)_2 + 2CH_3COOH$$

***6. Cacodyl Oxide Reaction.**—On mixing a dry acetate with a small quantity of **arsenious oxide** and heating in a test-tube, an extremely nauseous odour of **cacodyl oxide** is produced.

$$8CH_3 . COONa + As_4O_6$$

$$= 2(CH_3)_2As . O . As(CH_3)_2 + 4CO_2 + 4Na_2CO_3$$

This experiment should be conducted with great caution, and on a very small scale, as the fumes are **extremely poisonous.**

If, during the heating, the finger is held over the mouth of the test-tube, the smell is very noticeable on holding it to the nostril.

Detection of Formic and Acetic Acids in Presence of each other.

If the substance is a solution, part of it should be evaporated to dryness in order to apply the tests 1, 4, and 5. It should be borne in mind that, if the solution is acid, it must first be *neutralised* with sodium carbonate before evaporating to dryness.

I. Formic Acid.—1. Add to a small quantity of the solid substance a little cold concentrated sulphuric acid: **carbon monoxide** is evolved. (*Presence of formate.*)

2. Acidify part of the neutral solution *slightly* with dilute sulphuric acid, shake up with a little mercuric oxide, and filter. On boiling the solution reduction takes place. (*Presence of formate.*)

3. Warm a portion of the neutral solution with silver nitrate: reduction takes place. (*Presence of formate.*)

II. Acetic Acid.—4. Heat a small portion of the dry substance with arsenious oxide: a fœtid odour of **cacodyl oxide** is produced. (*Presence of acetate.*)

5. Act on a little of the substance with concentrated sulphuric acid, and warm very gently; as soon as no more carbon monoxide is evolved, add a little alcohol, and heat: a fruity odour of ethyl acetate produced. (*Presence of acetate.*)

If formic and acetic acid or their salts occur mixed with other organic acids or compounds which are not readily volatile, the mixture should be acidified with dilute sulphuric acid and distilled. The liquid in the receiver will contain the formic and acetic acids, and, after neutralisation, may be tested for them. The non-volatile substances will remain in the retort.

Lactic Acid (α-Hydroxy-propionic Acid).

$CH_3 . CH(OH)COOH$

There are three lactic acids, but the one most commonly occurring is the α or fermentation acid; the other sarco-lactic acid and ethylene lactic acid have, however, much the same properties, but whereas the α and sarco-lactic acids are optically active the ethylene lactic acid is inactive.

Lactic acid is a colourless, thick liquid, having rather the appearance of glycerol. It is odourless when pure, and has a strong acid taste. It cannot be distilled without decomposition. Lactic acid is soluble in water, alcohol, or ether in all proportions, but is insoluble in benzene, chloroform, or carbon disulphide.

1. On being heated in a dry test-tube irritating vapours are evolved.

***2. Potassium permanganate** is decolorised by solutions of lactic acid, effervescence taking place, and a smell of acetaldehyde being produced. The reaction is very vigorous with hot solutions.

3. On adding an equal volume of cold concentrated **sulphuric acid** to lactic acid, the mixture gets hot and commences to effervesce. On warming, charring takes place, and **carbon monoxide** is evolved.

***4.** When a mixture of lactic acid and 4 parts of dilute sulphuric acid (1 part concentrated acid and 2 parts water) is distilled, **acetaldehyde** and **formic acid** are produced, and may be tested for in the distillate.

$$CH_3 . CH(OH)COOH = CH_3 . CHO + H . COOH$$

5. Silver nitrate—but not Fehling's solution—is reduced by lactic acid.

6. Crystal Test.—One of the best methods to identify lactic acid in dilute solutions is to form the calcium or zinc salt, and to examine the crystals under the microscope. The zinc salt $(C_3H_5O_3)_2Zn, 3H_2O$, for example, may be prepared by digesting

the warm acid solution with zinc carbonate, filtering, and concentrating on the water bath. Quadratic crystals are obtained, which usually cluster together.

Oxalic Acid.

$$\begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array}$$

Colourless crystals, containing two molecules of water of crystallisation. Readily soluble in water and in alcohol. When heated to 100°, the crystalline acid melts in its own water of crystallisation; and, on further heating, sublimes. Most oxalates are insoluble in water.

1. When ignited, the oxalates of the alkaline metals and earths are converted into carbonates, with evolution of carbon monoxide.

$$\begin{array}{l}\mathrm{COOK}\\ |\\ \mathrm{COOK}\end{array} = \mathrm{CO} + \mathrm{K_2CO_3}$$

Those of the heavy metals produce an oxide, with evolution of carbon monoxide and dioxide.

$$\left.\begin{array}{l}\mathrm{COO}\\ |\\ \mathrm{COO}\end{array}\right\rangle \mathrm{Cu} = \mathrm{CO} + \mathrm{CO_2} + \mathrm{CuO}$$

Some few, such as **silver oxalate,** decompose into the metal and carbon dioxide.

$$\begin{array}{l}\mathrm{COOAg}\\ |\\ \mathrm{COOAg}\end{array} = 2\mathrm{Ag} + 2\mathrm{CO_2}$$

Pure oxalic acid, on being heated, volatilises completely, without charring. It partly sublimes unchanged, but when rapidly heated it splits up into carbon dioxide and formic acid.

$$\begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array} = \mathrm{CO_2} + \mathrm{H.COOH}$$

Part of the formic acid decomposes into carbon monoxide and water.

$$H.COOH = CO + H_2O$$

*2. **Concentrated sulphuric acid,** on heating, decomposes oxalic acid or oxalates, **carbon monoxide** and **carbon dioxide** being evolved: the presence of this latter being shown by passing the evolved gases through lime water. (Distinction from formates which only give carbon monoxide.)

$$\begin{array}{l}COOH\\ |\\ COOH\end{array} = CO + CO_2 + H_2O$$

3. **Silver nitrate** produces, with neutral solutions, a white crystalline precipitate of **silver oxalate,** soluble in ammonium hydroxide or nitric acid.

$$\begin{array}{l}COONa\\ |\\ COONa\end{array} + 2AgNO_3 = \begin{array}{l}COOAg\\ |\\ COOAg\end{array} + 2NaNO_3$$

*4. **Calcium chloride** gives, with neutral or alkaline solutions of oxalates, a white crystalline precipitate of **calcium oxalate,** insoluble in acetic acid, soluble in hydrochloric or nitric acid. This may be used as a crystal test.

$$\begin{array}{l}COONa\\ |\\ COONa\end{array} + CaCl_2 = \begin{array}{l}COO\diagdown\\ |\qquad\ \ Ca\\ COO\diagup\end{array} + 2NaCl$$

*5. On adding a solution of **potassium permanganate** to a solution of oxalic acid or an oxalate acidified with dilute sulphuric acid, and warming, the colour of the permanganate is destroyed, carbon dioxide being evolved.

$$5K_2C_2O_4 + 2KMnO_4 + 8H_2SO_4$$
$$= 6K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

Tartaric Acid.

$$\begin{array}{l} CH(OH)\,.\,COOH \\ | \\ CH(OH)\,.\,COOH \end{array}$$

Tartaric acid forms large colourless crystals which are readily soluble in water, moderately so in alcohol. Being a dibasic acid, it forms acid and neutral salts. The normal salts with the alkali metals, and most of the salts with metals of the iron group, are readily soluble in water. The acid salts of potassium and ammonium are difficultly soluble, the other acid salts readily soluble; while most other normal salts are insoluble, or only dissolve with difficulty.

***1.** Tartaric acid and tartrates char when heated, in the case of tartrates a carbonate or oxide of the metal being produced. During the charring, a strong smell resembling that of burnt sugar is produced.

***2.** Warm concentrated **sulphuric acid** decomposes tartrates, almost immediate charring taking place, with evolution of carbon monoxide, carbon dioxide, and sulphur dioxide.

***3. Silver nitrate** produces with neutral solutions a white precipitate of **silver tartrate,** soluble in excess of the tartrate, also in nitric acid or ammonium hydroxide.

$$\begin{array}{l} CH(OH)COOK \\ | \\ CH(OH)COOK \end{array} + 2AgNO_3 = \begin{array}{l} CH(OH)COOAg \\ | \\ CH(OH)COOAg \end{array} + 2KNO_3$$

On heating the ammoniacal solution of silver tartrate, it is reduced to metallic **silver.** The silver may be obtained in the form of a beautiful mirror on the sides of the test-tube if the following directions are followed: Carefully clean a test-tube with warm sodium hydroxide and distilled water; add ammonium hydroxide to the precipitated silver tartrate until it is almost (but not quite) dissolved; drop in a crystal of silver nitrate to the bottom of the test-tube and stand in a beaker of boiling water: in a short time, owing to the reduction

of the silver salt, a beautiful mirror of metallic silver forms on the sides of the tube.

***4. Calcium chloride** gives, with neutral solutions of tartrates, a white crystalline precipitate of **calcium tartrate.** Scratching the sides of the test-tube, and vigorous shaking, aid the precipitation, which, from dilute solutions, only takes place after some time. The precipitate is soluble in cold potassium, or sodium hydroxide, and in acetic acid.

$$\begin{array}{l}CH(OH)COOK\\ |\\ CH(OH)COOK\end{array} + CaCl_2 = \begin{array}{l}CH(OH)COO\\ |\\ CH(OH)COO\end{array}\!\!>Ca + 2KCl$$

***5. Potassium salts,** when added to tartaric acid or a tartrate, give (especially if the solution is well shaken and a little acetic acid is present) a colourless crystalline precipitate of **potassium-hydrogen tartrate.** With neutral salts, to obtain complete precipitation, it is necessary to add acetic acid, otherwise the acid tartrate is not formed. (*Cf.* Potassium, p. 128.)

$$\begin{array}{l}CH(OH)COONa\\ |\\ CH(OH)COONa\end{array} + KCl + CH_3.COOH = \begin{array}{l}CH(OH)COOK\\ |\\ CH(OH)COOH\end{array} + NaCl + CH_3.COONa$$

When potassium salts are added to free tartaric acid a precipitate is not produced in dilute solutions, unless sodium acetate is added to neutralise the mineral acid set free in the reaction.

$$\begin{array}{l}CH(OH)COOH\\ |\\ CH(OH)COOH\end{array} + KCl \rightleftharpoons \begin{array}{l}CH(OH)COOK\\ |\\ CH(OH)COOH\end{array} + HCl$$

From dilute solutions the precipitation only takes place after long standing. Presence of **boric acid** prevents precipitation.

***6. Drop Reaction.**—If a minute quantity of solid tartaric acid or a tartrate is mixed with twice its bulk of **resorcinol,** 2 drops of concentrated **sulphuric acid** added, and the mixture is *gently* warmed, a bright red coloration is produced. (Distinction from citrate.)

If **pyrogallol** is substituted for resorcinol, a fine violet-blue coloration is obtained. (Distinction from citrate.)

These reactions show best when extremely small quantities of tartaric acid or a tartrate are taken. *Great care must be taken not to heat too strongly*, otherwise charring takes place.

7. On adding a few drops of a solution of **ferrous sulphate** to a solution of a tartrate, then a few drops of **hydrogen peroxide,** and finally excess of sodium or potassium hydroxide, a violet to blue coloration is produced. (Distinction from citrate.)

Citric Acid.

$$C(OH)\begin{cases} CH_2 \cdot COOH \\ \cdot COOH + 2H_2O \\ CH_2 \cdot COOH \end{cases}$$

Citric acid forms colourless crystals, readily soluble in water and alcohol. The acid citrates are more soluble than the acid tartrates.

1. Citric acid or citrates carbonise when heated, acrid-smelling vapours being evolved.

***2.** When heated with concentrated **sulphuric acid,** citric acid and citrates evolve carbon monoxide and carbon dioxide. After some little time, the liquid becomes dark in colour, owing to charring, and sulphur dioxide is evolved. (Tartrates char almost immediately.)

***3. Silver nitrate** produces, with neutral solutions of citrates, a curdy white precipitate of **silver citrate,** soluble in ammonium hydroxide. On heating this solution no reduction takes place. (Distinction from tartrates.) But continued boiling causes slight reduction.

$$C_3H_4(OH)(COOK)_3 + 3AgNO_3 = C_3H_4(OH)(COOAg)_3 + 3KNO_3$$

***4. Calcium chloride,** when added to a neutral solution of a citrate, produces no precipitate in the cold (except after

standing some hours), but on boiling for several minutes a crystalline precipitate of **calcium citrate** is produced. The addition of caustic alkali causes immediate precipitation of calcium citrate, soluble in ammonium chloride, but on boiling the crystalline calcium citrate is precipitated, and is then no longer soluble in ammonium chloride.

$$2C_6H_5O_7K_3 + 3CaCl_2 = 3Ca(C_6H_5O_7)_2 + 6KCl$$

*5. **Cadmium chloride,** when added to neutral solutions, produces a white gelatinous precipitate of **cadmium citrate,** insoluble in hot water, readily soluble in hot acetic acid. (Cadmium salts give no precipitate with tartrates.)

$$2C_6H_5O_7K_3 + 3CdCl_2 = 3Cd(C_6H_5O_7)_2 + 6KCl$$

Cadmium citrate sometimes forms a transparent jelly.

*6. **Denigè's Test.**—Add to 2 c.c. of a solution of citric acid about 1 drop of mercuric sulphate solution (preparation, p. 371). Then add 5 to 6 drops of 2 per cent. $KMnO_4$. Decolorisation will take place, and then a white turbidity (due to a mixture of basic mercuric sulphate and mercury acetone dicarboxylate) will be produced. The amount of $KMnO_4$ to be added depends upon the concentration of the citric acid. Halogens should first be removed with $AgNO_3$. In presence of other organic compounds larger quantities of permanganate are required, just sufficient being added to leave a permanent faint pink. Sensitiveness 1 milligram.

Malic Acid.

$$\begin{array}{l} CH_2 . COOH \\ | \\ CH(OH)COOH \end{array}$$

Malic acid is found in the juice of many unripe fruits, including apples, and can be prepared from unripe mountain-ash berries. It is a crystalline solid, m.p. 100°. On being heated to 140-150° for some time, water is split off and fumaric

acid produced. The fumaric acid then sublimes when the mixture is heated to 200°, crystallising on the cool portions of the tube. When, however, the malic acid is rapidly heated to a high temperature, maleic anhydride distils over with water. The reaction in either case is represented by the following equation—

$$COOH . CH(OH) . CH_2 . COOH - H_2O$$
$$= COOH . CH : CH . COOH$$

The difference between fumaric and maleic acid is not shown in the equation, because they are steroisomers, *i.e.* they contain the same number of groups of the same kind, but these are arranged differently in space in three dimensions. For further information upon the subject, text-books on theoretical organic chemistry must be consulted.

Malic acid is readily soluble in both water and alcohol.

*1. **Calcium chloride,** in presence of excess of ammonium chloride and ammonium hydroxide, produces no precipitate, even on continued boiling. (Distinction from citric acid.) The addition, however, of two volumes of alcohol produces a white precipitate of calcium malate.

$$C_4H_4O_5Na_2 + CaCl_2 + 3H_2O = C_4H_4O_5Ca, 3H_2O + 2NaCl$$

Calcium malate is soluble in boiling lime water. (Distinction from citric acid.)

2. **Lead acetate** produces a white precipitate of lead malate.

$$C_4H_4O_5Na_2 + (CH_3 . COO)_2Pb + 3H_2O$$
$$= C_4H_4O_5Pb, 3H_2O + 2CH_3 . COONa$$

The precipitation is more complete from neutral salts of the acid. If the precipitate is boiled with water a portion goes into solution and a portion melts or becomes gummy. On cooling, the portion which has dissolved separates out again.

Separation of Oxalic, Citric, and Tartaric Acids (and Malic Acid).

Add excess of **calcium chloride** to a neutral solution, shake up, allow to stand for from twelve to fifteen minutes with occasional shaking, then filter and wash.

<table>
<tr>
<td colspan="2">Residue: This may be a mixture of calcium oxalate and tartrate. Boil with a little acetic acid, and filter.</td>
<td rowspan="2">Solution: Add a little more calcium chloride, and boil for three or four minutes. If a white precipitate gradually forms, the presence of
Citric Acid
is shown, which may be confirmed by filtering and warming with conc. H_2SO_4, when charring will slowly take place.†</td>
</tr>
<tr>
<td>Residue: Is calcium oxalate. Confirm by suspending in dilute sulphuric acid, warm to 60-70°, and add a dilute solution of potassium permanganate drop by drop. Decolorisation of the permanganate confirms
Oxalic Acid.</td>
<td>Solution: Evaporate to dryness on a water bath, and test for tartaric acid by warming a portion carefully with conc. H_2SO_4 and pyrogallol (§ 6, p. 256). A violet coloration shows the presence of
Tartaric Acid.
It may be further confirmed by § 3, p. 256.</td>
</tr>
</table>

Succinic Acid.

$$\begin{array}{l} CH_2\,.\,COOH \\ | \\ CH_2\,.\,COOH \end{array}$$

Colourless odourless crystals, m.p. 183°, b.p. 235°, with formation of succinic anhydride. Readily soluble in hot water or alcohol. Only slightly soluble in ether and insoluble in chloroform.

1. On strongly heating, succinic acid first melts and then boils, the vapours which are given off being extremely irritating.

2. Concentrated **sulphuric acid** dissolves succinic acid on warming without charring. On strongly heating, the solution becomes brown and sulphur dioxide is evolved.

† If **malic acid** is suspected, ammonium chloride and ammonia should be added before boiling: malic acid is not then precipitated. It can be detected after the calcium citrate has been precipitated by adding alcohol. Further, the precipitate of calcium malate is soluble in lime water.

*3. **Silver nitrate** produces a white precipitate of silver succinate from neutral solutions, readily soluble in ammonia.

$$C_2H_4(COONa)_2 + 2AgNO_3 = C_2H_4(COOAg)_2 + 2NaNO_3$$

*4. **Calcium chloride** produces from neutral solutions a white precipitate of calcium succinate. The precipitate is not usually produced at once, but comes down on standing a short time, especially upon shaking.

*5. **Ferric chloride** gives with neutral solutions a light brown precipitate of basic ferric succinate.

$$3C_2H_4(COONa)_2 + 2FeCl_3 + 2H_2O$$
$$= 2C_2H_4(COO)_2Fe . OH + 6NaCl + C_2H_4(COOH)_2$$

Benzoic Acid.

$$C_6H_5 . COOH$$

Benzoic acid forms colourless needles or small plates, possessing a slight but characteristic aromatic odour. It melts at 121°, and sublimes, boiling at 250°. Readily volatile with steam. Soluble in hot water, from which it crystallises on cooling, also in alcohol or ether. Benzoates are generally soluble in water.

*1. On heating benzoic acid it first begins to sublime, then melts, and finally gives off dense white fumes, which cause sneezing or coughing.

2. Benzoic acid and benzoates dissolve in strong sulphuric acid on warming, without evolution of gas, and without charring.

3. Dilute mineral acids, when added to aqueous solutions of benzoates, decompose them, and a white crystalline precipitate of benzoic acid is produced.

4. **Silver nitrate** produces from neutral solutions a white precipitate of **silver benzoate,** soluble in hot water, from which it recrystallises on cooling. The precipitate is readily soluble in ammonium hydroxide.

$$C_6H_5COONa + AgNO_3 = C_6H_5COOAg + NaNO_3$$

*5. **Ferric chloride** gives, with neutral solutions (see p. 266), a buff-coloured precipitate of basic **ferric benzoate.**

$$2C_6H_5COONa + FeCl_3 + H_2O = (CH_5COO)_2FeOH + 2NaCl + HCl$$

Citrates and tartrates hinder or prevent precipitation. Ferric benzoate is soluble in boiling water with difficulty, but if the solution is moderately dilute, it is not reprecipitated again on cooling. It is readily soluble in ammonium hydroxide (**Drop Reaction**).

*6. **Benzoic acid** or **benzoates,** when heated with about 1 c.c. of concentrated sulphuric acid and about an equal bulk of alcohol, produce a pleasant and distinctive aromatic odour of **ethyl benzoate.** On diluting the mixture with water, oily drops of ethyl benzoate separate out.

$$C_6H_5COOH + C_2H_5OH = C_6H_5COOC_2H_5 + H_2O$$

*7. On heating **benzoic acid,** or **benzoates,** with about four times their bulk of lime in a hard glass test-tube, benzene is produced, which can be recognised by its odour, and by the inflammability of its vapour.

$$C_6H_5COOH + Ca(OH)_2 = C_6H_6 + CaCO_3 + H_2O$$

A delicate confirmatory test may be made as follows: The test-tube in which the operation is carried out is fitted with a cork and delivery tube, and during the heating the end of the tube is made to dip below about 0·5 c.c. of conc. nitric acid and 1 drop of conc. sulphuric acid contained in another test-tube. The mixture is first gently, and then strongly heated, the cool sides of the tube being then warmed, in order to volatilise any condensed benzene vapour, and to cause it to pass into the nitric acid. The nitric acid is now diluted with water, when the characteristic odour of **nitrobenzene** is obtained.

$$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O$$

Salicylic Acid (Ortho-hydroxybenzoic Acid).

$$C_6H_4\left\langle\begin{matrix} OH & (1) \\ COOH & (2) \end{matrix}\right.$$

Colourless needle-shaped crystals, possessing no smell. Very slightly soluble in cold water, rather more so in hot. Readily soluble in ether or alcohol. The acid melts at 156°. Most salicylates are fairly soluble in water. The acid is soluble in sodium carbonate.

1. When heated in a dry tube **salicylic acid** first melts, and on further heating sublimes; when very rapidly heated it is decomposed into **phenol** and **carbon dioxide.**

$$C_6H_4\left\langle\begin{matrix} OH \\ COOH \end{matrix}\right. = C_6H_5OH + CO_2$$

2. Concentrated **sulphuric acid** dissolves salicylic acid and salicylates. On heating for some little time, the solution darkens, and finally gas is evolved.

3. Dilute mineral acids, when added to aqueous solutions of **salicylates,** decompose them, liberating salicylic acid, which separates out as a white crystalline precipitate.

***4.** On being strongly heated with lime an odour of phenol is produced.

$$C_6H_4\left\langle\begin{matrix} OH \\ COOH \end{matrix}\right. + Ca(OH)_2 = C_6H_5OH + CaCO_3 + H_2O$$

A characteristic blue coloration may be obtained by conducting the evolved phenol through a delivery tube into a little water, to which has been added one or two drops of ammonium hydroxide; then add a few drops of bromine water or a solution of bleaching powder, and gently warm. (*Cf.* § 3, p. 267.)

5. Silver nitrate produces in neutral solutions a white precipitate of **silver salicylate,** soluble in boiling water.

$$C_6H_4\left\langle\begin{matrix} OH \\ COONa \end{matrix}\right. + AgNO_3 = C_6H_4\left\langle\begin{matrix} OH \\ COOAg \end{matrix}\right. + NaNO_3$$

*6. **Ferric chloride** gives both with salicylic acid and salicylates an intense violet-red coloration, which vanishes on adding excess of mineral acids (**Drop Reaction**). Acetic acid, tartaric acid, citric acid, and most organic acids, when present in *large* excess, also prevent this coloration, but addition of a few drops of ammonia will cause it to appear. The coloration produced by phenol is destroyed by a small quantity of acetic acid. (See § 1, p. 266.)

7. **Bromine water** gives a white precipitate of **dibromsalicylic acid,** or **tribromsalicylic acid,** depending upon the quantity added.

8. On heating with concentrated nitric acid, salicylic acid and salicylates are converted into **picric acid,** with formation of a deep yellow solution, and, on adding excess of caustic soda, the coloration is intensified. If the solution is now boiled with a little dextrose, the colour changes to deep red, owing to the formation of picraminic acid.

*9. When salicylic acid or salicylates are mixed with about 1 c.c. of concentrated **sulphuric acid,** and about an equal quantity of **methyl alcohol,** and the mixture heated, the characteristic smell of **methyl salicylate,** " Oil of Wintergreen," is produced.

$$C_6H_4\begin{cases}OH\\COOH\end{cases} + CH_3 . OH = C_6H_4\begin{cases}OH\\COOCH_3\end{cases} + H_2O$$

Cinnamic Acid (*β*-Phenyl Acrylic Acid).

$$C_6H_5CH : CH . COOH$$

Cinnamic acid forms colourless pearly crystals, m.p. 133°. When rapidly heated it distils undecomposed at 300°. On slow distillation it is converted into *styrene* and carbon dioxide

$$C_6H_5CH : CH . COOH = C_6H_5CH : CH_2 + CO_2$$

Cinnamic acid is only slightly soluble in cold water, but dissolves readily in hot water and also in alcohol, ether, or

chloroform. Owing to its sparing solubility in water, it is precipitated by dilute acids from its alkali metal salts.

1. On mixing cinnamic acid or its salts with **lime,** and strongly heating, benzene is evolved, which may be recognised by the tests described under benzoic acid, § 7, p. 261.

***2. Calcium chloride** precipitates from neutral solutions white calcium cinnamate. The precipitate is soluble in boiling water, and crystallises out again on cooling.

$$2C_6H_5CH : CH . COOK + CaCl_2 = (C_6H_5CH : CH . COO)_2Ca + 2KCl$$

The precipitate shows a tendency to adhere to the sides of the test-tube. (Benzoic acid gives no precipitate with calcium chloride, hence the two acids may be separated by means of calcium chloride.)

***3. Ferric chloride** gives a light yellow precipitate of basic ferric cinnamate.

4. Silver nitrate, when added to neutral solutions of cinnamates, produces a white precipitate of silver cinnamate.

***5.** Oxidising agents, such as **potassium permanganate** or **persulphates,** when warmed with an alkaline solution of cinnamic acid, oxidise it to benzaldehyde, which may be readily detected by the smell.

Hippuric Acid (Benzoyl glycine).

$$C_6H_5 . CO . NH . CH_2 . COOH$$

Hippuric acid is a good example of an acid occurring in animal life, since it is present in the urine of horses. It forms colourless and odourless rhombic prisms or needles, m.p. 187·5°, difficultly soluble in cold water (1 : 600), more readily in hot water. It dissolves readily in alcohol, but only with difficulty in ether. It is insoluble in petroleum spirit, and may thus *be separated from benzoic acid, which is soluble in this solvent.*

1. On heating in a dry tube the acid first melts, then

becomes dark in colour, and a sublimate of benzoic acid is produced. The vapours have a smell reminiscent of benzaldehyde.

2. When ignited with soda lime, ammonia is evolved, which may be recognised by the reactions on p. 131.

***3. Ferric chloride** produces, from neutral solutions, a brownish-pink precipitate of ferric hippurate, which is soluble in alcohol.

***4. Silver nitrate** gives, from neutral solutions, a white curdy precipitate of silver hippurate, which is soluble in hot water, from which it crystallises on cooling in characteristic feathery tufts. It may be necessary to allow the solution to stand for a short time before it crystallises (**Crystal Test**).

$$C_6H_5 . CO . NH . CH_2 . COONa + AgNO_3 \\ = C_6H_5 . CO . NH . CH_2 . COOAg + NaNO_3$$

5. When boiled with potassium hydroxide (1 : 1) hippuric acid is hydrolysed into benzoic acid and glycine. The benzoic acid crystallises out on acidification, and may be recognised by any of the tests on p. 261.

$$\begin{array}{r|l} C_6H_5 . CO & . NH . CH_2 . COOH = C_6H_5 . COOH \\ HO & H \qquad + NH_2 . CH_2 . COOH \end{array}$$

Phenol (Carbolic Acid).

C_6H_5OH

Phenol forms colourless crystals; m.p. 43°, b.p. 182°. On adding 10 per cent. of water the crystals form a syrupy fluid. Phenol, or its solution, has a strong, sweetish odour; the smell is not characteristic, because other aromatic hydroxyl compounds, *e.g.* the cresols, have a very similar odour. It is soluble in caustic alkali to form a phenate, but not in alkali carbonates.

***1. Ferric chloride** produces a deep violet coloration; *small* quantities of hydrochloric acid or acetic acid destroy

the colour, turning it yellow. The ferric chloride should therefore be first neutralised (see p. 369).

***2. Bromine water,** even in very dilute solutions, gives a white precipitate of **tribromophenol,** soluble in caustic alkalis (**Drop Reaction**).

$$C_6H_5OH + 3Br_2 = C_6H_2Br_3OH + 3HBr$$

***3.** On adding to an aqueous solution of phenol a few drops of **ammonium hydroxide,** then a few drops of **bromine water,** and gently warming, a beautiful indigo blue coloration is produced. Hydrochloric acid, added to this solution, turns it red. In very dilute solutions the coloration is not immediate.

***4. Liebermann's Reaction.**—If about 1 c.c. of conc. **sulphuric acid,** and a small piece of **sodium** or **potassium nitrite** about the size of a pin's head are added to a small quantity of phenol, and the mixture gently warmed, a deep green or blue coloration is produced ; when this solution is poured into water, it turns red, and on adding excess of caustic alkali, the blue or green colour returns.

5. Diazo-Reaction.—A few drops of a dilute solution of sodium nitrite are added to a solution of sulphanilic acid, followed by two drops of dilute sulphuric acid, the mixture being kept cool under a flowing tap during this process. A slightly alkaline solution of phenol is then added when an orange-red colour develops. This reaction is a general test for phenols as well as for nitrites and amino compounds (*e.g.* sulphanilic acid), and the mechanism is fully explained in § 2, p. 321.

Separation of Benzoic and Salicylic Acids and Phenol.

Make the solution to be tested alkaline † with sodium carbonate : the benzoic and salicylic acids will form sodium

† If the solution is already alkaline, it should be first acidified with hydrochloric acid, in case the phenol may be present as a phenate.

salts. Phenol only forms a sodium salt with sodium hydroxide (p. 266). Extract the phenol from the solution by means of ether. The ethereal solution is best separated by means of a small separating funnel. A pipette will answer the purpose when a funnel is not obtainable.

<table>
<tr>
<td rowspan="2">Ethereal Solution: Evaporate or distil off the ether. The phenol remains behind, and may be confirmed by—
A. Dissolving a portion in water, and adding a few drops of ammonia and of bromine water, and gently warming: an indigo blue coloration, which turns red on addition of hydrochloric acid (p. 267), confirms
Phenol.
B. It may be further confirmed by Liebermann's reaction (§ 4, p. 267); or by C. Diazo reaction (§ 5, p. 267).</td>
<td colspan="2">Aqueous Solution: Neutralise exactly with hydrochloric acid, and add neutral ferric chloride (p. 369). A buff-coloured precipitate is produced. [The colour of the precipitate will be more or less masked by the violet colour produced by the salicylate, should this happen to be present.] Filter and wash.</td>
</tr>
<tr>
<td>Residue: Is ferric benzoate: confirm benzoic acid by drying the precipitate, and mixing with excess of soda lime or lime, in a hard glass test-tube fitted with a delivery tube. Heat strongly, holding the end of the delivery tube under about ½ c.c. of strong nitric acid. Dilute with large bulk of water, when the characteristic smell of nitrobenzene will be noticed (§ 2, p. 292). Confirmation of
Benzoic Acid.</td>
<td>Solution is violet owing to the presence of salicylic acid. Make alkaline with ammonia, and filter off the precipitated ferric hydroxide. Evaporate solution to dryness, and confirm salicylic acid by—
A. Warming a small portion of the residue with strong nitric acid: a yellow coloration, due to the formation of picric acid, which, on the addition of a few drops of sodium hydroxide (p. 264), becomes more intense.
B. The other portion may be heated with a little concentrated sulphuric acid and methyl alcohol, when the characteristic odour of "oil of winter-green" further confirms
Salicylic Acid.</td>
</tr>
</table>

Uric Acid.

$C_5H_4O_3N_4$

Colourless crystalline powder, insoluble in cold, only slightly soluble in hot water. Insoluble in alcohol or ether. Soluble

in alkaline solutions, or in solutions containing salts which have an alkaline reaction, *e.g.*—

$$Na_3PO_4 + C_5H_4O_3N_4 = NaH_2PO_4 + C_5H_2O_3N_4Na_2$$

1. On being heated, uric acid does not melt, but is decomposed with charring; **ammonia, cyanic acid,** and **hydrocyanic acid** being evolved.

2. Uric acid dissolves in cold concentrated sulphuric acid without charring; on heating, however, decomposition takes place, with evolution of carbon monoxide, carbon dioxide, and sulphur dioxide.

***3.** When heated in a dry tube with a little solid **sodium,** or **potassium hydroxide, ammonia** gas is evolved, and **sodium cyanide** is produced. On cooling and dissolving the fused mass in water the solution gives the reactions for hydrocyanic acid (p. 151).

4. When an alkaline solution of uric acid is added to **Fehling's solution,** a white precipitate of **cuprous urate** is formed on gently warming; on further heating, reduction with formation of red **cuprous oxide** takes place.

***5.** On dissolving a little uric acid in **sodium carbonate,** and allowing a few drops to fall on a piece of filter paper, moistened with silver nitrate, a black stain is immediately produced, owing to reduction of the silver nitrate. This is a very delicate reaction, even very dilute solutions producing a light brown or yellow mark.

***6. Murexide Reaction.**—Moisten a little uric acid with concentrated **nitric acid,** and evaporate in a porcelain dish to dryness on a water bath. A yellow, reddish-brown, or magenta residue is obtained, the colour varying according to the duration of heating. Remove from the water bath and cool, then add a drop of **ammonium hydroxide,** when the colour changes to violet, and, on adding a drop of **caustic soda,** the violet develops a deep blue shade. The coloration disappears on warming. (*Cf.* Caffeine, § 4, p. 346.)

Meconic Acid.

$C_5H(OH)[COOH]_2O_2$

This acid is of interest because it occurs in opium in combination with morphine, as **morphine meconate.** Its detection is, therefore, important in cases of opium poisoning. Meconic acid crystallises in small plates, or in rhombic prisms containing 3 mols. H_2O. It is sparingly soluble in cold, but readily soluble in hot water ; it is also readily soluble in alcohol.

1. When heated in a dry tube it gives up its water of crystallisation at 100°, and at 120° splits up into comenic acid ($C_6H_4O_5$) and carbon dioxide, and on further heating into pyromeconic acid. At higher temperatures it chars, and an odour rather resembling that produced by the charring of tartaric acid results.

2. Neither cold nor hot concentrated **sulphuric acid** produces a visible change.

***3. Silver nitrate** produces a light yellow flocculent precipitate of **silver meconate,** readily soluble in ammonia, with formation of a light yellow solution.

$$C_5H_2O_3(COONa)_2 + 2AgNO_3 = C_5H_2O_3(COOAg)_2 + 2NaNO_3$$

***4. Calcium chloride** slowly throws down a white silky crystalline precipitate of **calcium meconate,** which has a very characteristic appearance.

$$C_5H_2O_3(COONa)_2 + CaCl_2 = C_5H_2O_3(COO)_2Ca + 2NaCl$$

***5. Ferric chloride** produces a characteristic purplish-brown coloration. On boiling, a basic precipitate is produced, but not so readily as with ferric acetate or formate.

$$3C_7H_2O_7Na_2 + 2FeCl_3 = (C_7H_2O_7)_3Fe_2 + 6NaCl$$

Gallic Acid.†

$C_6H_2(OH)_3COOH$

Gallic acid forms light yellowish-brown crystals, containing 1 mol. H_2O. It is slightly soluble in cold water, readily in hot water. It is also soluble in alcohol, glycerol, or acetone, but only slightly in ether.

1. On heating with concentrated sulphuric acid, the solution first becomes green and then purple.

*2. **Ferric chloride** produces a deep blue coloration or precipitate, which is soluble in excess of the reagent, forming a green solution.

*3. **Ferrous sulphate** produces an azure blue coloration.

*4. An ammoniacal solution of **potassium ferricyanide** gives a red coloration, changing to brown.

*5. **Potassium cyanide** produces a pink coloration, which rapidly disappears. The colour reappears again on shaking with air.

*6. **Lime water** or a solution of **barium hydroxide** produces a blue precipitate ; small quantities give only a blue coloration. When the quantity is very small, a reddish colour is produced, which changes to a dirty brown.

Gallotannic Acid† (Tannin, Tannic Acid).

$C_{14}H_{10}O_9$

Tannic acid, when pure, forms a colourless amorphous mass ; but it often occurs in commerce in the form of so-called needles. It is, however, generally of a yellowish appearance. It has a very astringent taste. It is readily soluble in water, especially on warming. Hydrochloric and sulphuric acids precipitate it from its solutions. Tannic acid

† The reactions of gallic and tannic acids refer to solutions of the free acids, and not of their salts, as with the other acids.

is easily soluble in dilute alcohol, but almost insoluble in absolute alcohol or ether.

1. Alkaline solutions of tannic acid rapidly oxidise in the air, becoming dark brown.

*2. On adding a solution of **gelatine** to a solution of tannic acid, a white or buff-coloured flocculent precipitate is produced. (Distinction from **gallic acid** and **pyrogallol.**)

*3. **Ferric chloride** gives a greenish-black precipitate of **ferric-gallotannate** (the basis of many blue-black inks).

*4. **Lime water** produces a grey precipitate.

*5. **Potassium cyanide** forms a brownish-red coloration, which becomes brown, assuming the red tint again on being shaken with air.

*6. **Ferrous sulphate** produces a dark violet coloration.

*7. **Lead nitrate** precipitates white **lead tannate.** Neither gallic acid nor pyrogallol gives a precipitate with lead nitrate, although they give precipitates with lead acetate.

8. An ammoniacal solution of **potassium ferricyanide** produces a deep red colour, changing to brown. A large excess of the reagent should not be added.

Pyrogallol (Pyrogallic Acid).

$C_6H_3(OH)_3$

Pyrogallol forms fine colourless needles, m.p. 133°, b.p. 293°. It is extremely soluble in water, alcohol, or ether, but not so readily in chloroform or benzene. It is an active poison, the symptoms being similar to those of phosphorus.

*1. **Alkaline solutions** of pyrogallol rapidly become brown, owing to absorption of oxygen. For this reason alkaline solutions of pyrogallol are employed in gas analyses for determining oxygen.

*2. **Lime water** produces a purple coloration, which quickly becomes brown.

*3. **Fehling's solution** is reduced on heating, while solutions of **silver** are immediately reduced in the cold: hence use of pyrogallol in photography.

*4. Dissolve a little pyrogallol in about 1 c.c. of water, add one or two drops of **formaldehyde** (formalin), and then about 2 c.c. of concentrated hydrochloric acid. On standing a few minutes, a white precipitate, which rapidly turns red, and, finally, a deep purple, is produced. (*Cf.* Formaldehyde, § 4, p. 300.)

*5. **Ferric chloride** produces a reddish-brown coloration.

*6. **Potassium cyanide** forms a brownish-red coloration; the solution gradually turns brown, but the red tint appears on shaking with air.

*7. **Ferrous sulphate** gives a brilliant purple-blue coloration.

SYNOPTIC TABLE SHOWING BEHAVIOUR OF GALLIC AND TANNIC ACIDS AND PYROGALLOL WITH VARIOUS REAGENTS.

Reagent.	Gallic acid.	Tannic acid.	Pyrogallol.
1. Concentrated sulphuric acid, on warming	1. First green, then bright purple	1. Darkens on strongly heating, becoming purple	1. Colourless solution, darkening on strongly heating
2. Lime water	2. Blue precipitate or coloration	2. Grey precipitate	2. Purple coloration, rapidly turning brown
3. Ferric chloride	3. Blue precipitate, soluble in excess to a green solution	3. Bluish-black precipitate (ink)	3. Reddish-brown coloration
4. Ferrous sulphate	4. Azure blue coloration	4. Blackish-violet coloration.	4. Azure blue coloration
5. Potassium cyanide	5. Pink coloration, quickly disappearing, returning on shaking with air	5. Brownish-red coloration, turning brown. Red tint reappearing on shaking with air	5. Brownish-red coloration, turning brown. Red tint reappearing on shaking with air
6. Lead nitrate	6. —	6. White precipitate	6. —
7. Solution of gelatine.	7. —	7. White precipitate	7. —

General Method of Procedure in Testing for Organic Acids.

It is hardly possible to give a table for the separation of all the organic acids which may be met with in analysis, but by the following method of procedure a fair idea of what acids are present may be obtained, and then special tests and separations may be applied. These reactions may be applied to the original substance, or to the substance treated as described on p. 246, and evaporated to dryness.

I. Tests in the Dry Way.

Test.	Observation.	Inference.
1. Heat a small portion of the substance in a dry tube	(*a*) A sublimate is produced	Benzoate, cinnamate, salicylate, succinate, malate
	(*b*) It chars, and an odour resembling that of burnt sugar is produced	Tartrate, hippurate, oxalate, meconate
	(*c*) Chars, and acrid vapours evolved	Citrate, lactate, succinate
	(*d*) Ammonia and hydrocyanic acid evolved	Urate, cyanides
2. Heat a small portion with soda-lime	(*a*) Inflammable vapours of benzene evolved	Benzoate, cinnamate
	(*b*) Vapours of phenol given off	Phenate, salicylate
	(*c*) Ammonia given off	Urate, hippurate
	(*d*) Inflammable gases	Formate, acetate, oxalate
3. Heat the substances with a little dilute sulphuric acid	Acid fumes evolved	Acetate, formate, lactate
4. Heat with concentrated sulphuric acid	(*a*) Smell of acetic acid	Acetate
	(*b*) CO evolved	Formate (in the cold), lactate
	(*c*) CO and CO_2 evolved without charring	Oxalate, urate
	(*d*) Blackening with evolution of CO, CO_2, and SO_2	Tartrate
	(*e*) Blackening after some little time with evolution of CO, CO_2, and SO_2	Citrate, succinate, salicylate
	(*f*) Solution becomes green and then purple	Gallate

II. Tests in Solution.

These tests should be applied to small portions of the neutral solution, prepared as described on p. 246.

Test.	Observation.	Inference.
1. Dilute sulphuric acid	White precipitate	Benzoate, cinnamate, salicylate
2. Ferric chloride	(*a*) Red coloration	Acetate, formate
	(*b*) Violet coloration	Salicylate, meconate
	(*c*) Bluish-black	Tannate, gallate
	(*d*) Buff - coloured precipitate	Benzoate
	(*e*) Light brown gelatinous precipitate	Succinate
	(*f*) Light yellow precipitate	Cinnamate
	(*g*) Greenish-black	Tannate
	(*h*) Brownish-pink	Hippurate
	(*i*) Reddish-brown	Pyrogallol
3. Acidify with acetic acid, and add calcium chloride	White precipitate	Oxalate, cinnamate
4. Add calcium chloride to neutral solution, shake up, and allow to stand a few minutes	White precipitate	Tartrate: If this is filtered off and the solution boiled for some minutes, a further precipitate may indicate a citrate. Calcium succinate is also slowly precipitated
		Precipitate is soluble in lime water—Malate
5. Cadmium chloride	(*a*) White crystalline precipitate	Oxalate, meconate
	(*b*) Gelatinous precipitate	Citrate
6. Solution of gelatine	White precipitate	Tannate
7. Lime water	(*a*) Blue coloration or precipitate	Gallate
	(*b*) White precipitate	Tannate
	(*c*) Purple coloration, becoming rapidly brown	Pyrogallol

By means of the above tests a very fair idea of what acids have to be looked for will be obtained. It is obvious, if **ferric chloride** produces no coloration, that formic and acetic acids

are absent. It must, however, be borne in mind that the violet coloration due to salicylic acid or phenol will mask the red coloration given by formic and acetic acids. Again, if **calcium chloride** produces no precipitate in an acetic acid solution, it will be waste of time to apply tests for an oxalate.

CHAPTER XIII.

ESTERS.

THE esters may be divided into two classes—

(1) those derived from organic acids in which the hydrogen atom in the carboxyl is replaced by an alkyl or aromatic radical;

(2) those in which the hydrogen atom of an inorganic acid is replaced by an alkyl or aromatic radical (ethereal salts).

I.—Esters derived from Organic Acids.

The ethereal salts all have a sweet and fruity smell, most of the odours being quite characteristic. Thus amyl acetate smells like pear-drops; ethyl acetate resembles apples; and methyl butyrate smells like pineapples.

In order to identify the esters of organic acids, the boiling-point is first taken, and then they are hydrolysed by boiling under a reflux condenser with a strong solution of potassium hydroxide, *e.g.*—

(1) $CH_3COOC_2H_5 + KOH = CH_3COOK + C_2H_5OH$

(2) $C_4H_9COOC_2H_5 + KOH = C_4H_9COOK + C_2H_5OH$

The alcohol is then distilled off and tested for in the distillate. The acid is obtained by evaporating the residue to small bulk, and then acidifying with hydrochloric acid. Or the alkaline solution is carefully neutralised, evaporated to dryness, and the neutral salt so obtained is employed to test for the acids.

For example, suppose that the substance to be examined is ethyl acetate (see (1) above). Ethyl alcohol will be found in

the distillate after hydrolysing and distilling, and may be tested for by any of the typical reactions—such, for instance, as the iodoform reaction, or by conversion into aldehyde (p. 300).

The solution on neutralisation and evaporation to dryness will give the characteristic tests for acetic acid.

The following table gives a few of the more common esters with their boiling-points :—

Ester.	Formula.	Boiling-point.
Methyl formate . . .	$H.COOCH_3$	32·5°
„ acetate . . .	$CH_3.COOCH_3$	57·5°
Ethyl formate . . .	$H.COOC_2H_5$	54·5°
„ acetate . . .	$CH_3COOC_2H_5$	76-77°
„ butyrate . . .	$C_3H_7COOC_2H_5$	121°
„ benzoate . . .	$C_6H_5COOC_2H_5$	212°
„ salicylate . . .	$C_6H_4(OH)COOC_2H_5$	231°
Amyl acetate . . .	$CH_3COOC_5H_{11}$	148°
Methyl salicylate . . .	$C_6H_4(OH)COOCH_3$	224°

II.—Ethereal Salts derived from Inorganic Acids.

These usually have a sweetish smell and taste, but the odour is not generally so fruity as that of the esters of organic acids. The nitrites, when inhaled, have the peculiar property of causing the face to flush.

On warming with moderately strong solutions of alkali hydroxides, they are hydrolysed, with formation of an alcohol and the alkali salt of the inorganic acid, thus—

$$C_2H_5NO_3 + KOH = C_2H_5OH + KNO_3$$
$$C_2H_5HSO_4 + NaOH = C_2H_5OH + NaHSO_4$$

A portion of the solution may be tested for the alcohol, or, better, the alcohol may be distilled off and tested for separately, the residue being tested for the inorganic acid. Before, however, decomposing the ester, its boiling-point should be determined, p. 236.

The mercaptans and sulphides are ethereal salts of hydrogen

sulphide and are readily recognised by their penetrating and objectionable smells.

Below are tabulated a few of the more common esters with their boiling-points and specific gravities :—

Ester.	Formula.	Boiling-point.	Sp. gr.
Methyl iodide . . .	CH_3I	43°	2·30
Ethyl bromide . . .	C_2H_5Br	39°	1·47
,, iodide . . .	C_2H_5I	72°	1·975
,, nitrite . . .	$C_2H_5NO_2$	16·5°	0·900
,, nitrate . . .	$C_2H_5NO_3$	87°	1·11
,, hydrogen sulphate .	$\begin{matrix}C_2H_5\\H\end{matrix}>SO_4$	—	—
Dimethyl sulphate . .	$SO_4(OCH_3)_2$	188°	—
Ethyl mercaptan . . .	C_2H_5SH	36°	0·839
,, sulphide . . .	$(C_2H_5)_2S$	91°	0·837
Propyl chloride . . .	C_3H_7Cl	45°	0·896
,, bromide . . .	C_3H_7Br	71°	1·362
,, iodide . . .	C_3H_7I	102°	1·743
Isopropyl chloride . .	$(CH_3)_2CHCl$	36·5°	0·859
,, bromide . .	$(CH_3)_2CHBr$	59·5°	1·31
,, iodide . . .	$(CH_3)_2CHI$	89·5°	1·703
Amyl nitrite . . .	$C_5H_{11}NO_2$	97-99°	0·88

On treating the **nitrites** with a reducing agent, *e.g.* tin and hydrochloric acid, they are reduced to the alcohol—

$$C_2H_5O\,.\,NO + 6H = C_2H_5OH + NH_3 + H_2O$$

The **nitrates**, on the other hand, are not reduced by this treatment.

Nitroparaffins.

The nitroparaffins cannot be compared with the above types of nitrates and nitrites. In the nitrites the nitrogen is attached to the alkyl radical through the oxygen atom R . O . NO, but in the nitro-paraffins the linkage is through the nitrogen atom $R\,.\,N\begin{matrix}\nearrow O\\ \searrow O\end{matrix}$. In the first case the nitrogen is trivalent, and in the second pentavalent. The nitro-compounds may dissolve in caustic alkalis, but are not decomposed by them, as is the case with the nitrites, which are readily hydrolysed.

On reduction with tin and hydrochloric acid the nitroparaffins are converted into amines—

$$C_2H_5NO_2 + 6H = C_2H_5NH_2 + 2H_2O$$

The amines form hydrochlorides, but on making the reduced solution alkaline, the characteristic amine smell is noticed, and the amine can be obtained from the solution by steam-distillation. To test for the amine the distillate is exactly neutralised with hydrochloric acid, and evaporated to dryness on the water bath, when the hydrochloride of the amine is obtained in the solid condition. A portion of the residue can be used to show the carbylamine reaction (see p. 281). This reaction, however, can be shown with the crude mixture of the tin salt and amine, by making alkaline with alcoholic potash, and warming with a little chloroform.

In order to find which alkyl radical was present, pour off the reduced solution from any tin remaining, and add a little sodium nitrite to the acid solution. The amine will be converted into the alcohol, thus—

$$C_2H_5NH_2 + HO.NO = C_2H_5OH + H_2O + N_2$$

Distil off a portion of the solution, and test the distillate for the alcohol.

The reduction test is easily carried out, by taking three or four drops of the nitroparaffin in a test-tube, adding 2 or 3 c.c. of caustic alkali, and a small piece of zinc. On gently warming, the characteristic fishy smell of the amine thus produced is noticed. Further, a piece of moistened red litmus paper held in the mouth of the test-tube is turned blue.

Chloroform.

$CHCl_3$

Chloroform is a colourless neutral fluid with a characteristic ethereal odour, almost insoluble in water, but readily soluble in alcohol or ether. It boils at 60-62°, sp. gr. 1·49, and when

the vapour is allowed to come into contact with the flame of a Bunsen burner, it colours the edges green.

1. Carbylamine Reaction.—When heated with a few drops of aniline and 2 or 3 c.c. of alcoholic potash, the characteristic and disgusting odour of **phenyl isonitrile** (carbylamine) is produced.

$$CHCl_3 + 3(KOH)† + C_6H_5NH_2$$
$$= C_6H_5N \vdots C + 3KCl + 3H_2O$$

2. Alcoholic Potash.—On warming for a few minutes with a few c.c. of alcoholic potash the chloroform is decomposed, and if the solution so obtained is diluted with water, acidified with nitric acid, and a solution of silver nitrate added, a white precipitate of silver chloride is produced.

$$CHCl_3 + 4(KOH) = H \cdot COOK + 3KCl + 2H_2O$$

If the silver chloride is filtered off, and the solution neutralised and warmed, the formate will reduce the excess of silver salt. (*Cf.* p. 248.)

3. Fehling's Solution.—When chloroform is warmed with alkaline copper solutions (p. 370), a precipitate of yellowish-red cuprous oxide is produced.

$$CHCl_3 + 2Cu(OH)_2 + 5KOH$$
$$= Cu_2O + K_2CO_3 + 3KCl + 5H_2O$$

Chloral hydrate behaves in a similar manner, because when it is warmed with alkalis, chloroform is produced.

$$CCl_3CH(OH)_2 + KOH = CHCl_3 + HCOOK + H_2O$$

4. On covering a little powdered resorcinol with a few drops of chloroform, then with about 0·5 c.c. of a strong solution of alkali hydroxide and warming, a brilliant reddish coloration is produced.

† KOH is placed in brackets to indicate that it is an alcoholic solution.

Carbon Tetrachloride.

CCl_4

Colourless, heavy, and pleasant-smelling liquid; it boils at 77°; sp. gr. 1·608.

1. It is decomposed when heated with alcoholic potash.

$$CCl_4 + 4(KOH) = 4KCl + CO_2 + 2H_2O$$

On acidifying the solution with nitric acid, carbon dioxide is evolved, which may be tested for in the usual manner. Silver nitrate also gives a precipitate of silver chloride.

2. Distinction from Chloroform.—It does not give the carbylamine reaction.

Iodoform.

CHI_3

Forms small yellow hexagonal tablets or yellowish leaflets, m.p. 119°, which have a peculiar and characteristic odour. It is almost insoluble in water, but is distinctly volatile in steam. It dissolves readily in alcohol, acetone, or ether.

1. On heating with sodium, it gives the reactions for iodine (see p. 234).

2. Cover a little powdered iodoform with a few drops of phenol, and carefully warm with a small piece of sodium hydroxide. A red coloration is produced, and on dissolving in alcohol a very intense red solution is obtained.

Iodoform is such a characteristic substance that, if the melting-point is taken and the substance proved to contain iodine, it is hardly necessary to try any further reactions.

The Amines.

The amines may be regarded as ammonia in which one or more of the hydrogen atoms have been replaced by alkyl radicals. They are called Primary, Secondary, or Tertiary,

according to whether one, two, or three hydrogen atoms have been replaced; thus—

NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$
Ammonia	Methylamine (Primary)	Dimethylamine (Secondary)	Trimethylamine (Tertiary)

They also form compounds corresponding to ammonium salts and to ammonium hydroxide.

NH_4Cl	$(CH_3)_3N \cdot HCl$	$(CH_3)_3N{<}^{CH_3}_{OH}$
Ammonium chloride.	Trimethyl ammonium chloride.	Tetramethylammonium hydroxide.

By means of certain specific reactions one is able to determine whether the amine belongs to the primary, secondary, etc., class.

Primary Amines.—**1.** When warmed with a mixture of chloroform and alcoholic potassium hydroxide they form isonitriles (isocyanides). The isonitrile, or **carbylamine** reaction, depends upon the offensive odour which the carbylamines possess (see p. 281).

$$CH_3NH_2 + CHCl_3 + 3(KOH) = CH_3NC + 3KCl + 3H_2O$$
$$C_6H_5NH_2 + CHCl_3 + 3(KOH) = C_6H_5NC + 3KCl + 3H_2O$$

2. On dissolving the amine in a little dilute hydrochloric acid and adding a small quantity of sodium nitrite, the amine is decomposed with formation of an alcohol (from which it may be identified) and liberation of nitrogen, thus—

$$C_2H_5NH_2 + HO.NO = C_2H_5OH + N_2 + H_2O$$

3. Hydrochloroplatinic acid or **Hydroauric acid** produces yellow crystalline precipitates when added to solutions of primary amines acidified with hydrochloric acid.

$$CH_3NH_2 + HAuCl_4 = CH_3.NH_2, HAuCl_4$$

Secondary Amines.—These do not give the carbylamine reaction, neither are they converted into alcohols by nitrous acid, but form **nitrosoamines.**

$$(C_2H_5)_2NH + HO.NO = (C_2H_5)_2N.NO + H_2O$$

Dissolve the secondary amine in a little dilute hydrochloric acid, and slowly add an aqueous solution of potassium or sodium nitrite, taking care that the mixture does not become hot. An oily nitrosoamine gradually separates out; extract this with a little ether, wash with dilute sodium carbonate, and to a portion of the ethereal solution apply **Liebermann's** test (p. 267).

Mix the solution with a few crystals of phenol and then cover with a few c.c. of concentrated sulphuric acid. A dark green solution will be obtained, which on diluting with water becomes red, and on dilution and addition of excess of sodium hydroxide, assumes an intense blue or green colour.

2. **Hydrochloroplatinic acid** or **Hydroauric acid** gives an orange-coloured precipitate when added to solutions of secondary amines acidified with hydrochloric acid.

$$(C_2H_5)_2NH + H_2PtCl_6 = [(C_2H_5)_2NH]_2, H_2PtCl_6$$
$$(C_2H_5)_2NH + HAuCl_4 = (C_2H_5)_2NH, HAuCl_4$$

Tertiary amines do not give the carbylamine reaction, neither do they form nitrosoamines. The tertiary amines, like the secondary amines, are powerful bases and precipitate metallic hydroxides from solutions of the metallic salts; for example, ferric hydroxide from ferric chloride. To show this reaction it is best to make the solution of the amine alkaline with sodium hydroxide and to distil a few cubic centimetres; the distillate will contain the amine, which has an alkaline reaction, and precipitates ferric hydroxide.

The tertiary amines also unite directly with alkyl halogen compounds, forming crystalline quaternary salts, *e.g.*

$$(CH_3)_3N + CH_3I = (CH_3)_4NI$$

Extract a portion of the alkaline solution of a tertiary amine with ether, dry the ethereal solution with a little calcium chloride, and add a few drops of ethyl iodide to it: a white crystalline precipitate will show the presence of the quaternary compound. If the pure tertiary amine is to hand, the ethyl

iodide may be directly added to it, when union will take place with great rise in temperature.

Quaternary Salts.—These are colourless and odourless. The iodide may, however, be brownish in colour, owing to slight decomposition.

They are not decomposed by boiling with alkaline hydroxides, but when aqueous solutions are shaken with freshly precipitated silver hydroxide,† the free quaternary bases are obtained, a precipitate of the silver salt of the halogen being also produced.

$$(CH_3)_4NI + AgOH = (CH_3)_4N . OH + AgI$$

The solution will be strongly alkaline, and will liberate ammonia from a solution of ammonium chloride or another salt of ammonia.

Halogen Fatty Acids.

(Chloro-acetic acids.)

In describing the halogen acids the compounds of acetic acid only will be dealt with, because the properties of all of the halogen acids are very similar.

Acetic acid forms three chloro acids depending upon whether one, two, or three of the methane hydrogens are replaced by chlorine. Strange to say, the mono and trichloroacetic acids are crystalline solids, but the dichloroacetic acid is a liquid at ordinary temperatures.

		M.P.	B.P.
Monochloroacetic Acid,	$CH_2ClCOOH$	63°	185-187°
Dichloroacetic ,,	$CHCl_2COOH$	4°	189-191°
Trichloroacetic ,,	CCl_3COOH	52°	195°

In general properties these acids are very similar, forming neutral salts with alkalis. When the aqueous solutions are

† To prepare silver hydroxide, add a slight excess of sodium hydroxide to a solution of silver nitrate. Filter off the hydroxide and wash with water until free from alkali. The hydroxide may now be used without being dried.

treated with a solution of silver nitrate, no precipitate of silver chloride is produced, although from strong solutions the silver salt of the acid may separate out, *e.g.*

$$CH_2ClCOONa + AgNO_3 = CH_2ClCOOAg + NaNO_3$$

Monochloroacetic Acid.

This acid melts at 63°, but if the temperature of the bath is raised to 70° and then cooled until the acid solidifies in the capillary, on again raising the temperature it melts at 52°.

Monochloroacetic acid dissolves readily in water, a considerable lowering of temperature taking place.

Alkali Hydroxides.—On gently heating with sodium or potassium hydroxide, the acid is converted into glycollic acid. Addition of silver nitrate to a portion of the solution, acidified with nitric acid, gives a precipitate of silver chloride.

$$CH_2ClCOOK + KOH = CH_2(OH)COOK + KCl$$

Dichloroacetic Acid

is a liquid at ordinary temperatures. When the silver salt is boiled in a small quantity of water for some little time with silver hydroxide, it is decomposed, silver chloride and glyoxalic acid being produced.

$$\begin{matrix} CHCl_2 \\ | \\ COOAg \end{matrix} + AgOH = \begin{matrix} CHO \\ | \\ COOH \end{matrix} + 2AgCl$$

The solution after separation by decantation from the silver chloride, gives Schiff's reaction (p. 305) and reduces Fehling's solution and ammoniacal silver nitrate.

The silver salt of dichloroacetic acid very rapidly darkens on exposure to light.

Trichloroacetic Acid

on warming with alkalis gives chloroform and carbon dioxide (carbonates).

$$CCl_3COOK + KOH = CHCl_3 + K_2CO_3$$

If the solution is now warmed with aniline and alcoholic potash, the carbylamine reaction is given.

It is, perhaps, better to carry out this reaction in one stage by heating the trichloroacetic acid with alcoholic potash and aniline.

Lead Acetate.—Forms a lead salt which is readily soluble in water, but is precipitated on addition of alcohol.

Amides.

Amides may be looked upon as being carboxylic acids in which the OH group of the carboxyl is replaced by the amino group NH_2; or as derivatives of ammonia in which one of the hydrogen atoms is replaced by an acetyl, benzoyl, etc., radical, as the case may be. They are usually prepared by the interaction of an acid chloride or anhydride with ammonia; also by dry distillation of the ammonium salt of a fatty acid. As examples of this class of compound, we will take acetamide, oxamide, and benzamide.

Acetamide.

$$CH_3CONH_2$$

Place about 1 c.c. of acetic anhydride or acetyl chloride in a test-tube, and cautiously add, drop by drop, concentrated ammonia, until the vigorous reaction ceases. On cooling, acetamide will crystallise out. The acetamide may be melted and poured from the test-tube into an evaporating basin. When solid, it is spread upon a porous plate to drain. It melts at 80-82°, and boils at 222°; has an unpleasant "mousy" odour, and is readily soluble in water or alcohol.

1. On heating with dilute acids or alkalis, it is decomposed into acetic acid and ammonia.

$$CH_3CONH_2 + H_2O = CH_3COOH + NH_3$$

If acids are employed, ammonia can afterwards be detected by the addition of sodium hydroxide. If the hydrolysis is carried out by means of alkalis, the ammonia escapes during the hydrolysis. The acetic acid can be detected on distillation after acidification with dilute sulphuric acid.

2. On heating with phosphorus pentoxide, water is split off and methyl cyanide (acetonitrile) produced; b.p. 81·6°.

$$CH_3CONH_2 - H_2O = CH_3CN$$

Oxamide.

$$\begin{array}{l} CO\,.\,NH_2 \\ | \\ CO\,.\,NH_2 \end{array}$$

Dissolve a few c.c. of ethyl or methyl oxalate in alcohol, and add a slight excess of concentrated ammonia. Almost immediately a white precipitate of oxamide is produced.

$$\begin{array}{l} COO\,.\,CH_3 \\ | \\ COO\,.\,CH_3 \end{array} + 2NH_3 = \begin{array}{l} CO\,.\,NH_2 \\ | \\ CO\,.\,NH_2 \end{array} + 2CH_3OH$$

Oxamide is a white powder, almost insoluble in water, alcohol, or ether. It sublimes on heating without melting, but is partially decomposed during the operation.

1. On heating with dilute acids or alkalis, oxamide is hydrolysed with formation of oxalic acid and ammonia.

$$\begin{array}{l} CO\,.\,NH_2 \\ | \\ CO\,.\,NH_2 \end{array} + 2H_2O = \begin{array}{l} COOH \\ | \\ COOH \end{array} + 2NH_3$$

The ammonia can be detected as usual, and the hydrolysed solution, after acidification with dilute sulphuric acid, will at once decolorise permanganate.

2. On heating with phosphorus pentoxide, dehydration ensues with formation of cyanogen, which will burn at the mouth of the test-tube with a peach-coloured flame.

$$\begin{array}{l} CO\,.\,NH_2 \\ | \\ CO\,.\,NH_2 \end{array} - 2H_2O = C_2N_2$$

Benzamide.

$$C_6H_5CONH_2$$

Place 1 c.c. of benzoyl chloride in a test-tube and cautiously add, drop by drop, excess of concentrated ammonia. Benzamide will crystallise out and can be recrystallised by boiling with water. It melts at 128° and is a colourless solid, sparingly soluble in cold water but readily in hot.

1. On hydrolysis with acids or alkalis, ammonia and benzoic acid are produced.

$$C_6H_5CONH_2 + H_2O = C_6H_5COOH + NH_3$$

If hydrolysed with alkalis, ammonia is given off during hydrolysis, and benzoic acid is precipitated out on acidifying.

Phosphorus pentoxide produces phenyl cyanide, which has a smell resembling benzaldehyde. (Caution, it is very poisonous.)

$$C_6H_5CONH_2 - H_2O = C_6H_5CN$$

Methyl and Ethyl Oxalate.

Methyl oxalate is a colourless crystalline solid, m.p. 54°, b.p. 163°. It is readily soluble in water, alcohol, and ether.

Ethyl oxalate is a colourless liquid, boiling at 186°; it is practically insoluble in water.

1. On hydrolysis with acids or alkalis, oxalic acid and the corresponding alcohol are produced. The alcohol can be

distilled off and tested for separately. The solution contains oxalic acid.

$$\begin{array}{l} COO \,.\, CH_3 \\ | \\ COO \,.\, CH_3 \end{array} + 2H_2O = \begin{array}{l} COOH \\ | \\ COOH \end{array} + 2CH_3OH$$

2. On dissolving in alcohol and adding concentrated ammonia, oxamide is produced.

$$\begin{array}{l} COOCH_3 \\ | \\ COOCH_3 \end{array} + 2NH_3 = \begin{array}{l} CO \,.\, NH_2 \\ | \\ CO \,.\, NH_2 \end{array} + 2CH_3OH$$

CHAPTER XIV.

HYDROCARBONS, HIGHER FATTY ACIDS, AND GLYCERIDES.

Hydrocarbons.

It is important to distinguish between hydrocarbons of the **paraffin** series and of the **benzene** series :—

Paraffins.

The paraffins may either be liquids, solids or semi-solids (greases), *e.g.* paraffin oil, paraffin wax, and vaselin. They are not very soluble in alcohol, but are readily soluble in ether, chloroform, or carbon disulphide; they are insoluble in water.

Use ligroïn or kerosene for the reactions.

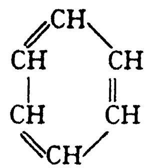
1. Concentrated **sulphuric acid** or a mixture of 2 parts sulphuric acid and 1 part strong nitric acid, has no action upon the paraffins in the cold.

2. On boiling with a strong aqueous solution of sodium hydroxide the oil does not dissolve, and on adding a strong solution of salt no precipitate of soap is produced, whereas with saponifiable oils, such as olive oil or butter, a soluble soap is produced by the action of hot alkali.

3. Bromine water is not decolorised when shaken up with the paraffins.

4. Phenol is insoluble in the paraffins, but dissolves in aromatic hydrocarbons.

Benzene.



Benzene is a colourless fluid which is insoluble in water, but readily soluble in the majority of organic solvents, such as alcohol, ether, etc. It freezes at 6° and boils at 80·5°.

1. Pure benzene does not impart any colour to concentrated **sulphuric acid,** but, generally speaking, owing to the presence of thiophen in commercial benzene, the acid is coloured brown, and the addition of a trace of a nitrite changes the colour to violet.

2. To 5 c.c. of a mixture of 2 parts conc. sulphuric acid and 1 part conc. nitric acid, add drop by drop 2 c.c. of benzene with continual shaking. If the mixture gets hot, cool between each addition of benzene. Place the vessel containing the mixture into a hot water bath for about five minutes, and then pour into an excess of water. Oily yellow drops of nitrobenzene will sink to the bottom of the water.

$$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O$$

The nitrobenzene (oil of mirbane) has a smell rather resembling that of benzaldehyde; the latter is therefore sometimes adulterated with nitrobenzene.

Bromine, when added to benzene, colours it brown; gradually the mixture becomes warm, and hydrobromic acid is evolved. The reaction is more rapid and energetic if the mixture is warmed, or if a piece of aluminium foil, coated with mercury, is placed in the mixture.

Toluene.

$C_6H_5 . CH_3$

Colourless, rather pleasant-smelling fluid, b.p. 111°. Insoluble in water, but readily soluble in ether, alcohol, acetone, chloroform, etc.

Detection in presence of benzene. Heat the hydrocarbon with a mixture of 1 part of a saturated solution of potassium dichromate and 4 parts conc. sulphuric acid. The toluene is oxidised to benzoic acid. Dilute the solution with water, and extract three or four times with ether. On evaporating off the ether the benzoic acid is obtained, and the tests on p. 261 may be applied.

A few drops of **bromine,** when added to a little toluene dissolved in chloroform, colour it brown, but the mixture gradually gets warm and vapours of hydrobromic acid are evolved. The greater the number of alkyl groups which the hydrocarbon of the benzene series contains, the more vigorous is the reaction with bromine.

Higher Fatty Acids.

Palmitic acid—$C_{15}H_{31}COOH$; m.p. 62·6°.
Stearic acid—$C_{17}H_{35}COOH$; m.p. 69·3°.
Oleic acid—$C_{17}H_{33}COOH$; m.p. 14·0°.

These acids all occur naturally, in the form of their glycerine esters, in fats or oils. Hard fats usually contain considerable quantities of the glycerides of stearic (stearin) and palmitic acids (palmitin) ; soft and liquid fats contain the glyceride of oleic acid (olein). In order to obtain the acids for testing purposes, a small quantity of a fat may be saponified.

Add about 10 grms. of fat to a solution of 6-7 grms. of potassium hydroxide in 20 c.c. of water and 40-50 c.c. of alcohol. Fit the flask which contains this mixture with an

upright condenser, and boil until a few drops of the solution dissolve completely in distilled water; evaporate off the alcohol and redissolve the residue in water. The solution now contains the alkali salt of the acid together with glycerol.

To obtain the free acid, pour into water, and acidify with dilute hydrochloric acid. Stearic and palmitic acids separate as flocculent solids, oleic acid as an oil. Wash several times on a filter paper with warm water. The solid acids can be separated from the oleic acid by pressing between filter papers and then crystallising from alcohol. The oleic or other oily acid can be obtained from the filter paper by extracting with ether.

Reactions of Glycerol Esters (Fats).

1. Heat a few drops of the fat with 1 or 2 grms. of solid sodium bisulphite. Characteristic acid odour of acrolein is produced. (See § 3, p. 309.)

2. When dropped upon paper a greasy stain is left, which is not removed by heating on the water bath.

***3.** Make a mixture of 5 c.c. of alcohol and 10 c.c. of ether, and add one drop of phenolphthalein, then add two or three drops of a normal solution of caustic alkali. On now shaking up with the fat, the red colour produced by the alkali remains. Free fatty acids decolorise such a solution.

Reactions of Free Acids.

1. The melted acids, when dropped upon paper, leave a greasy stain, which is not removed by heating on the water bath.

***2.** When treated with phenolphthalein, as in § 3 above, the acid discharges the red colour.

***3.** On warming with a concentrated solution of sodium carbonate, the acid dissolves. On cooling, the mixture sets to a solid or jelly-like mass (soap). Fats do not dissolve when treated in this manner.

*4. Warm 1 or 2 grms. of the fatty acid with 100 c.c. of distilled water, and carefully add caustic alkali until most, but *not* quite all, the acid has dissolved. Filter off the undissolved portion.

(*a*) Shake up a few drops of this solution with distilled water: a soapy lather is produced.

(*b*) *Lead acetate* gives a white precipitate of the lead salt —lead plaster—which, on warming, becomes plastic.

(*c*) Phenol, and the higher phenols which are insoluble in water, readily dissolve in this solution.

(*d*) Acids reprecipitate the free fatty acid.

The main difference in the reactions between *oleic* and palmitic and stearic acids is due to the fact that oleic acid is unsaturated, and therefore takes up bromine by addition. If a small quantity of each of these three acids is dissolved in chloroform, and then a few drops of a dilute solution of **bromine** in chloroform or carbon tetrachloride is added, then only the solution containing the oleic acid will decolorise the bromine.

The alkali salts of oleic acid also reduce and decolorise a solution of **potassium permanganate**, whereas the salts of stearic and palmitic acids have no action.

Detection of Benzene Hydrocarbons in Presence of Paraffin Hydrocarbons.

Unless the boiling-points of the hydrocarbons are some distance apart, it is not possible to separate them by fractional distillation.

A rough separation may be made by shaking the mixture up with 95 per cent. alcohol, which completely dissolves the benzene hydrocarbons but has very slight solvent action upon the paraffins. The mixture separates into two layers, one being a solution of the benzene hydrocarbon in alcohol, the other mainly the paraffin. The layers are separated by means of a separating funnel, and then separately shaken up with an

excess of water. On now applying tests, one layer (generally the upper) will be found to consist mainly of the paraffin hydrocarbon, and the other of the benzene hydrocarbon.

(*a*) The most certain method of detection is to treat the mixture with fuming sulphuric acid. The benzene hydrocarbon is converted into a sulphonate, which is soluble in water, the paraffin being unaffected. If it is desired to recover the aromatic hydrocarbon, the aqueous solution, after separation of the paraffin, is treated with excess of lime, the mixture evaporated to dryness, and the calcium salt subjected to dry distillation, when the hydrocarbon distils over.

(*b*) In some cases the sodium salt of the sulphonic acid can be obtained by pouring the strong acid solution into a saturated solution of sodium chloride when the salt separates out, and may be filtered off. The paraffin hydrocarbon floats upon the surface of the aqueous solution,† and may be separated.

(*c*) Another way is to treat the mixture of hydrocarbons with a mixture of equal volumes of concentrated nitric and sulphuric acids. Allow to stand for some time, cooling, if the reaction becomes too vigorous; and, finally, when reaction has ceased, heat on the water bath for a few minutes. Pour into cold water, and then separate the oily layer from the aqueous layer. The nitro compound is now reduced with tin and hydrochloric acid until its smell has vanished. The amino compound so produced remains dissolved in the acid solution. The paraffin floats on the surface and can be removed with a separating funnel. The amino compound can then be obtained by rendering the acid solution alkaline, and extracting with ether.

When a fatty oil, such as olive or linseed oil, is mixed with paraffin or aromatic hydrocarbons, the method of separation becomes rather complicated. It is first necessary to saponify as described on p. 293. The mixture is then poured into an excess of a saturated salt solution, and steam-distilled. The

† A mixture of benzene and ligroïn is easily separated by this method.

sodium salt of the fatty acid remains behind, and the unsaponifiable oils distil over with the steam, and may then be identified in any appropriate manner.

Naphthalene.

$C_{10}H_8$

Naphthalene has a characteristic smell, and forms white pearly plates which melt at 80°, and boil at 218°; but it volatilises at all temperatures. It is readily soluble in alcohol, ether, benzene, or most organic solvents. It burns with a smoky, luminous flame.

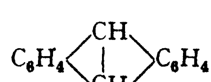
1. Picric Acid.—On dissolving naphthalene in alcohol and adding the solution to a strong alcoholic solution of picric acid, yellow needle-shaped crystals of naphthalene picrate separate out [$C_{10}H_8, C_6H_2(NO_2)_3OH$]; m.p. 150°.

2. Naphthaquinone.—Dissolve about 1 grm. of naphthalene in a few c.c. of hot glacial acetic acid, and, keeping hot, add, drop by drop, a strong solution of potassium permanganate, until the red colour of the permanganate is no longer destroyed. On pouring into water, naphthaquinone separates out and may be crystallised from alcohol or glacial acetic acid. Yellow crystals, m.p. 125°, with the characteristic odour of quinones.

$$C_{10}H_8 + 3O = C_{10}H_6O_2 + H_2O$$

3. Cover a trace of naphthalene with a drop of ferric chloride, and then drop on it concentrated sulphuric acid. A reddish colour changing to lilac is produced.

Anthracene.



Anthracene is odourless, and forms colourless lustrous plates which have a blue fluorescence, m.p. 213°, b.p. 351°,

readily soluble in hot benzene, but only sparingly soluble in alcohol or ether, moderately soluble in hot acetone.

1. Picric Acid.—When anthracene is dissolved in hot acetone, and a strong solution of picric acid in acetone is added to it, ruby-red needle-shaped crystals of **anthracene picrate** ($C_{14}H_{10}$, $C_6H_2(NO_2)_3OH$) separate out, m.p. 138°. An excess of alcohol decomposes the picrate.

2. Anthraquinone.—Dissolve about 1 grm. of anthracene in a few c.c. of boiling glacial acetic acid, and add to it a concentrated solution of chromic acid in glacial acetic acid, or a strong solution of potassium permanganate until the purple colour of the permanganate is no longer discharged. On pouring into water, anthraquinone separates out, and may be recrystallised from benzene, m.p. 286°.

$$C_6H_4\left\langle\begin{matrix}CH\\ |\\ CH\end{matrix}\right\rangle C_6H_4 + 3O = C_6H_4\left\langle\begin{matrix}CO\\ \\ CO\end{matrix}\right\rangle C_6H_4 + H_2O$$

When finely powdered anthraquinone is treated with zinc-dust and dilute sodium hydroxide and the mixture boiled, a deep red coloration is produced; on shaking with air the solution is decolorised.

The reaction depends on the formation of **oxanthrol** by reduction.

$$C_6H_4\left\langle\begin{matrix}—CO—\\ \\ CH(OH)\end{matrix}\right\rangle C_6H_4$$

This dissolves in the sodium hydroxide, producing the red coloration. On oxidation with air it is reconverted into anthraquinone.

CHAPTER XV.

ALDEHYDES, ALCOHOLS, ACETONE, GLYCEROL.

THE aldehydes contain the monovalent group CHO, the hydrogen and oxygen of which are not present as hydroxyl, but are attached separately to the carbon atoms thus $-C\begin{matrix} /\!\!/ O \\ \backslash H \end{matrix}$ The aldehydes are powerful reducing agents, owing to the ease with which they take up an atom of oxygen, being oxidised to acids (compare the ketones, p. 307). They are obtained by the oxidation of primary alcohols; therefore, as some of the tests for alcohols depend upon this oxidation, the reactions of **aldehydes** are placed before those of the alcohols.

Formaldehyde.

H . CHO

Formaldehyde is a gas which, at low temperatures, can be condensed to a liquid. It has a peculiar sharp odour. If a solution of formaldehyde is evaporated on the water bath, it is converted into a white solid cake of **paraformaldehyde.** A 40 per cent. solution of formaldehyde is marketed under the name of "**formalin.**"

*__1.__ On adding formaldehyde to an ammoniacal solution of silver nitrate, and placing the test-tube containing the mixture in a beaker of boiling water, a brilliant silver mirror is obtained.

$$H . CHO + Ag_2O = H . COOH + 2Ag$$

2. Fehling's solution is reduced by formaldehyde on warming, a red deposit of cuprous oxide being produced.

$$H . CHO + 2CuO = H . COOH + Cu_2O$$

***3. Schiff's Reaction.**—To a dilute solution of the dye **fuchsine**, which has been rendered colourless by means of sulphurous acid, add a little formaldehyde; in a few seconds the solution becomes coloured pink, the coloration becoming very intense on standing.

***4.** If a freshly prepared solution of **pyrogallol** is added to a solution of formaldehyde, which is then strongly acidified with concentrated **hydrochloric acid**, in a few minutes (five or ten minutes if the solution is extremely dilute) a white precipitate is produced, which rapidly turns pink, and finally a deep magenta red.

***5. Phenylhydrazine Hydrochloride.**—This may be prepared as required by adding two or three drops of **phenylhydrazine** to about 7 c.c. of water, and acidifying with dilute hydrochloric acid. In carrying out the test, take about 1 c.c. of this solution and add an equal volume of a fresh dilute solution of **sodium nitro-prusside**, then about 2 c.c. of the solution to be tested, and finally an excess of sodium hydroxide, when an intense blue colour results.

Alternatively, 5 c.c. of solution are heated in a water-bath for five minutes with 1 c.c. of reagent, and after cooling, 0·5 c.c. of 5 per cent. potassium ferricyanide is added followed by 2 c.c. of concentrated hydrochloric acid. A purple-red colour, which may be extracted with ether, is produced.

Acetaldehyde (Aldehyde).

$CH_3 . CHO$

Acetaldehyde is a colourless liquid, possessing a characteristic odour. It boils at 21°, and is inflammable. It is soluble in water, alcohol, or ether in all proportions.

A solution which shows the reactions of the aldehyde may be prepared by oxidising alcohol with **potassium dichromate** and sulphuric acid, as described on p. 305; or by adding two

or three drops (not more) of concentrated sulphuric acid to about 20 c.c. of **paraldehyde,** and cautiously distilling.

***1.** An ammoniacal solution of **silver nitrate** is reduced by acetaldehyde on warming with formation of a silver mirror. The experiment is carried out as described under formaldehyde.

***2. Fehling's solution** is reduced on warming, red cuprous oxide being deposited. (Aromatic aldehydes do not reduce alkaline copper salts.)

***3. Schiff's Reaction.**—With a decolorised solution of fuchsine, acetaldehyde behaves like formaldehyde. (See § 3, p. 300.)

4. If a freshly prepared, fairly strong solution of **pyrogallol,** containing excess of concentrated **hydrochloric acid,** is added to a solution of aldehyde, a white precipitate, which gradually turns slightly yellow, is produced on standing. In the case of very dilute solutions, the precipitate appears only after some time. (*Cf.* Formaldehyde, § 4, p. 300.)

5. On warming with an equal volume of strong sodium hydroxide a yellowish-brown resinous mass (aldehyde resin) is produced. (*Cf.* § 3, p. 302.)

6. On shaking with a concentrated solution of **sodium bisulphite** a colourless crystalline compound is produced, $CH_3 . CH(OH)SO_3Na$. From dilute solutions the substance only separates out after standing for some time.

Benzaldehyde.

$CH_5 . CHO$

When freshly distilled, benzaldehyde is a colourless, highly-refractive oily liquid, but on keeping it becomes light yellow. It is readily soluble in the usual organic solvents, but only slightly soluble in water, to which, however, it imparts its characteristic smell of bitter almonds. B.p. 179°. Bitter almond oil of the pharmacy contains the glucoside **emulsin,** and on warming with dilute alkalis, the aqueous solution gives

the reactions for cyanides (p. 151) and for dextrose (p. 312), after the benzaldehyde has been extracted with ether.

*1. Ammoniacal **silver nitrate** is reduced by benzaldehyde, and, on warming, a brilliant silver mirror is produced. Alkaline copper solutions are *not* reduced by benzaldehyde. (*Cf.* Acetaldehyde.)

*2. A saturated solution of **sodium hydrogen sulphite** gives on shaking up with benzaldehyde a white crystalline compound.

$$C_6H_5 . C\begin{matrix}\diagup O \\ \diagdown H\end{matrix} + NaHSO_3 = C_6H_5CH\begin{matrix}\diagup OH \\ \diagdown O . SO_2Na\end{matrix}$$

The aldehyde is liberated again by warming with a solution of sodium carbonate.

*3. When shaken up with an excess of a strong solution of **caustic alkali**, benzaldehyde is converted (more rapidly on warming) into an equimolecular mixture of benzoic acid and benzyl alcohol.

$$2C_6H_5CHO + KOH = C_6H_5 . COOK + C_6H_5 . CH_2OH$$

The alcohol can be removed by extraction with ether; it boils at 206°, and the benzoic acid may be recognised in the aqueous solution (p. 261).

It should be noted that, when aldehydes of the aliphatic series are warmed with caustic alkali, a resinous substance (aldehyde resin) is produced (see § 5, p. 301).

Detection of Nitrobenzene in Presence of Benzaldehyde.

Shake the mixture up with sodium bisulphite. The benzaldehyde unites with the bisulphite (*cf.* § 2, above), forming a white crystalline mass. The nitrobenzene remains in solution, from which it can be extracted by means of ether. If the nitrobenzene is then mixed with dilute sulphuric acid, and reduced by adding a few small pieces of zinc, it is

converted into aniline, which may be tested for, after making the solution alkaline and extracting with ether, by the reactions on p. 320.

Chloral Hydrate.

$$CCl_3 . CH\begin{matrix} \diagup OH \\ \\ \diagdown OH \end{matrix}$$

Sharp-smelling colourless crystals, soluble in water, alcohol, ether, chloroform, and most organic solvents. It melts at 57°, and boils at 97·5°.

*1. When about 2 c.c. of concentrated **sulphuric acid** are added to about 2 grms. of chloral hydrate, water is absorbed, and liquid chloral floats upon the surface of the acid.

*2. On gently warming with **sodium hydroxide,** chloral hydrate is decomposed into chloroform and formic acid.

$$CCl_3 . CH\begin{matrix} \diagup OH \\ \\ \diagdown OH \end{matrix} = CHCl_3 + H . COOH$$

The solution may be tested for formates (p. 247). If the quantity of chloral hydrate taken is not too small, the chloroform separates out as a layer below the aqueous solution.

*3. **Ammoniacal silver nitrate** is reduced by chloral hydrate, with formation of a silver mirror.

*4. **Silver nitrate** gives no precipitate of silver chloride, but if the solution of chloral hydrate is acidified with dilute sulphuric acid, a small piece of zinc added, and the mixture allowed to stand a few minutes, the addition of silver nitrate now produces a white precipitate of silver chloride.

5. Schiff's reagent is not coloured when added to a solution of chloral hydrate. But phenylhydrazine and sodium hydrogen sulphite both react in the usual manner.

Methyl Alcohol.

CH_3OH

Methyl alcohol is a colourless neutral liquid, boiling at 66°. It is soluble in water in all proportions. When mixed with water, contraction of volume takes place, the mixture at the same time becoming warm. Commercial methyl alcohol often contains acetone, in which case it gives the iodoform reaction. (See Acetone, p. 307.)

***1.** On adding methyl alcohol to a small quantity of a formate, then about an equal volume of concentrated sulphuric acid, and warming, the distinctive odour of **methyl formate** is noticed.

$$CH_3OH + H.COOH = H.COOCH_3 + H_2O$$

***2. Formic Acid Test.**—Place about 3 or 4 grms. of powdered **potassium dichromate** into a small flask fitted with a fairly long delivery tube, and cover the dichromate with water. Now add the alcohol, which has previously been mixed with an equal volume of 50 per cent. sulphuric acid. Allow to stand for three or four minutes, dilute with an equal bulk of water, and distil into a test-tube.

Neutralise the distillate with sodium carbonate, and boil vigorously for about one minute in order to drive off any formaldehyde or acetaldehyde (which may have been produced if ethyl alcohol was present). Divide the solution into two parts. To the first portion add **ferric chloride,** when a red coloration will be produced. To the second portion add silver nitrate, and warm : reduction will take place, a black or brown deposit being obtained.

The following equations express the reactions which take place. The alcohol is first oxidised to formaldehyde, which is immediately further oxidised to formic acid.

$$(a)\quad CH_3.OH + O = H.CHO + H_2O$$
$$(b)\quad H.CHO + O = H.COOH$$

Ethyl Alcohol.

C_2H_5OH

Ethyl alcohol is a colourless inflammable liquid, boiling at 78·4°. It is miscible with water in all proportions with contraction of bulk (48 c.c. of water and 52 c.c. of alcohol giving only 96 c.c., after being mixed).

***1.** On heating a little alcohol with an **acetate** and concentrated **sulphuric acid,** the characteristic fruity odour of **ethyl acetate** is given off.

$$C_2H_5OH + CH_3 . COOH = CH_3 . COOC_2H_5 + H_2O$$

***2. Iodoform Reaction.**—To an aqueous solution of alcohol add a few small crystals of **iodine,** or a few drops of a solution of iodine in potassium iodide; warm gently, and add drop by drop a solution of sodium hydroxide or carbonate, till the brown colour due to the iodine has disappeared. On cooling, a yellow crystalline precipitate of **iodoform** is produced. When the alcoholic solution is very dilute, no immediate precipitation takes place, but the peculiar and very characteristic smell of iodoform is noticeable (see also Acetone, § 1, p. 307).

$$C_2H_5OH + 5I_2 + 7KOH = CHI_3 + CO_2 + 7KI + 6H_2O$$

***3. Aldehyde Test.**—When heated with sulphuric acid and potassium dichromate, ethyl alcohol is not converted into acetic acid, but is merely oxidised to acetaldehyde. The reaction is carried out as already described in § 2, under Methyl Alcohol; and the aldehyde, which is best collected by distilling into a small quantity of water in a test-tube, is tested for by means of **Schiff's reaction** (p. 300), and by reduction of an ammoniacal solution of silver nitrate with production of a silver mirror.

$$C_2H_5OH + O = CH_3CHO + H_2O$$

4. Oxidation with **potassium permanganate.** When ethyl alcohol is heated with a solution of potassium permanganate,

the colour of the permanganate disappears. On acidifying the mixture with dilute sulphuric acid and distilling, the distillate will be found to have an acid reaction, and will answer to the test for acetic acid (p. 249).

Detection of Methyl and Ethyl Alcohols when they occur together.

1. **Methyl alcohol** may be detected in presence of **ethyl alcohol** by the action of sulphuric acid and potassium dichromate, which oxidises it to **formic acid**.

2. **Ethyl alcohol**, by the **iodoform** reaction, and by the formation of **acetaldehyde**, when warmed with potassium dichromate and sulphuric acid, and of acetic acid when warmed with potassium permanganate.

Amyl Alcohol (Isobutyl Carbinol).

$$\begin{matrix} CH_3 \searrow & \\ & CH \,.\, CH_2 \,.\, CH_2 \,.\, OH \\ CH_3 \nearrow & \end{matrix}$$

Amyl alcohol is the chief constituent of fusel oil, and is a colourless, rather oily liquid, b.p. 132°, with a characteristic odour. It is only slightly soluble in water.

1. Concentrated **sulphuric acid**, added to amyl alcohol, causes it to turn red or reddish-brown, when the mixture is gently warmed.

*2. On adding concentrated **sulphuric acid**, and a small quantity of **acetic acid** or of an **acetate**, to amyl alcohol, and then gently warming, an odour of essence of pears, **amyl acetate**, is produced. The smell is more marked on pouring the mixture into excess of water.

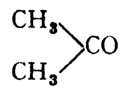
$$C_5H_{11}OH + CH_3COOH = CH_3COOC_5H_{11} + H_2O$$

*3. When heated with **potassium dichromate** and **sulphuric acid**, as already described under Methyl Alcohol, § 1, p. 304, a pleasant fruity odour of **amyl valerianate** is produced,

($C_4H_9COOC_5H_{11}$). The odour is better distinguished on pouring into water.

4. When amyl alcohol is heated with an equal volume of concentrated **sulphuric acid** until it just turns brown, then about half a volume of glacial **acetic acid** and 1 c.c. of **ferric chloride** added, and the mixture again heated, a brilliant violet coloration is produced.

Acetone.



Acetone is a colourless inflammable liquid, having a pleasant ethereal smell. It is miscible with water, alcohol, or ether in all proportions; b.p. 56·3°. It is one of the ketones, since it contains the —C : O group, and unlike the aldehydes these do not react with Fehling's solution, silver nitrate or Schiff's reagent.

***1. Iodoform Reaction.**—Add to a solution of acetone a few crystals of iodine, or a solution of iodine in potassium iodide; then carefully add sodium hydroxide or carbonate till the brown colour of the iodine disappears, and warm gently. On cooling, iodoform separates out in small golden-yellow plates.

$$(CH_3)_2CO + 6I_2 + 8KOH$$
$$= 2CHI_3 + K_2CO_3 + 6H_2O + 6KI$$

This reaction is also given by ethyl alcohol. If, however, a solution of acetone is made alkaline with ammonia, which should not be added in large excess, and then a solution of iodine in potassium iodide added drop by drop, until a small quantity of a black precipitate of nitrogen iodide is formed, on gently warming the black precipitate disappears, and iodoform crystallises out. *Under these conditions ethyl alcohol does not give the iodoform reaction.*

2. On mixing a few drops of a freshly prepared solution of **sodium nitroprusside** with a solution of acetone, adding **ammonia,** and shaking, a violet or violet-red coloration is produced. The colour disappears on warming, but reappears on cooling.

*3. **Gunning's Reaction.**—If a solution of acetone is added to one of **mercuric chloride,** and **sodium hydroxide** is then added drop by drop, a yellow precipitate of mercuric oxide is formed, which immediately dissolves again. If the quantity of acetone is very small, so much precipitate may be formed that only partial solution will take place. In this case filter through a double filter paper; it may be necessary to filter more than once. Acidify the clear solution so obtained with hydrochloric acid, and add a little **stannous chloride:** a white or grey precipitate will be produced. This reaction depends upon the fact that mercuric oxide is soluble in acetone.

*4. When shaken up with a concentrated solution of **sodium bisulphite,** a white crystalline addition product is produced.

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO + \begin{matrix}H\\Na\end{matrix}\!\!>SO_3 = \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C<\!\!\begin{matrix}OH\\SO_3Na\end{matrix}$$

Glycerol (Glycerine).

$$\begin{matrix}CH_2 \,.\, OH\\ | \\ CH \,.\, OH\\ | \\ CH_2 \,.\, OH\end{matrix}$$

Glycerol is a colourless, odourless, viscid fluid, which has a sweet taste. It boils at 290° with decomposition. Glycerol is readily soluble in water or alcohol, but insoluble in chloroform or ether. It is neutral to litmus.

1. Cold, concentrated **sulphuric acid** produces no change of colour with glycerol; and even when they are heated together on a water bath, only a slight yellow coloration is produced. (Distinction from a solution of cane sugar.)

2. Potassium or **sodium hydroxide** produces no change of colour, even on boiling. (Distinction from a solution of dextrose.)

***3.** Powdered **potassium hydrogen sulphate,** when heated with glycerol, produces acrid vapours of **acrolein.**

$$C_3H_5(OH)_3 = CH_2 : CH . CHO + 2H_2O$$

If the reaction is carried out in a test-tube fitted with a delivery tube, and the acrolein passed into water, a solution of acrolein is obtained which shows the usual tests for aldehydes, reducing ammoniacal silver with formation of a mirror, and colouring a decolorised solution of fuchsine. (Schiff's reaction, p. 300.)

***4.** On adding to a 1 per cent. solution of borax a few drops of phenolphthalein, a pink coloration is produced; the addition of glycerol causes the pink coloration to disappear, but it reappears on warming, again vanishing on cooling. (Ammonium salts also cause this coloration to be destroyed, but it does not reappear on warming. Dextrose and other polyhydric alcohols also give this reaction, though not so markedly as glycerol. See p. 312.)

Before testing a solution for glycerol, it should be evaporated to small bulk on the water bath. Should sugar be present, it must be removed. This is best done by evaporating to dryness on a water bath with lime and sand, then extracting the powdered mass with a mixture of equal volumes of absolute alcohol and ether. After distilling or evaporating off the alcohol and ether, the necessary tests may be applied.

Allyl Alcohol.

$$CH_2 : CH . CH_2 . OH$$

Pungent, colourless liquid, b.p. 96°. Miscible in water in all proportions, but can be salted out with potassium carbonate.

1. Being an unsaturated compound, it shows reactions peculiar to such substances. It decolorises bromine water

when this is added drop by drop to the alcohol or its aqueous solution.

$$CH_2 : CH . CH_2 . OH + Br_2 = CH_2Br . CHBr . CH_2OH.$$

2. A cold dilute solution of alkaline permanganate is reduced and thus decolorised. The permanganate solution should be sufficiently diluted with water to render it transparent and then rendered alkaline with sodium carbonate.

3. Acetyl chloride when added to the alcohol forms the ester. Shake up with dilute sodium carbonate to remove the excess of the acetyl chloride, when the characteristic odour of the allyl acetate is noticed.

$$CH_2 : CH . CH_2OH + CH_3COCl$$
$$= CH_2 : CH . CH_2O . COCH_3 + HCl$$

CHAPTER XVI.

THE CARBOHYDRATES AND SACCHARIN.

THE sugars belong to the class of organic compounds called the carbohydrates. They all contain carbon, oxygen, and hydrogen, the oxygen and hydrogen occurring in them in the proportion in which they are found in water, *i.e.* two atoms of hydrogen to one atom of oxygen. In the case of dextrose, for example, $C_6H_{12}O_6$ may be considered as $C_6 + 6H_2O$.

Saccharin, although not a sugar, has been placed in this chapter owing to its extreme sweetness (400 times that of cane sugar).

When sugars which contain an aldehyde or a ketone group are treated with phenylhydrazine, they are converted into **hydrazones**; thus glucose forms **glucose-phenylhydrazone.**

$$CH_2(OH)(CH.OH)_4.CHO + C_6H_5NH.NH_2$$
$$= CH_2(OH)(CH.OH)_4CH:N.NHC_6H_5 + H_2O$$

If, however, excess of phenylhydrazine is employed, the —CH.OH group next to the —CHO group becomes oxidised to —CO, part of the phenylhydrazine being reduced to aniline and ammonia.

$$C_6H_5.NH.NH_2 + 2H = C_6H_5NH_2 + NH_3$$

The oxidation product of the phenylhydrazone then combines with a second molecule of phenylhydrazine, with formation of an **osazone.**

$$CH_2(OH)(CH.OH)_3CO.CH:N.NH.C_6H_5 + C_6H_5.NH.NH_2$$
$$=CH_2(OH)(CH.OH)_3.C(N.NHC_6H_5).CH:N.NH.C_6H_5+H_2O$$

As the preparation of the osazones has been of great value in identifying and isolating the sugars, the method of formation is here given.

About half a gram of the sugar is dissolved in 5–6 c.c. of water, and 2–3 grms. of **phenylhydrazine** added, then about 3 c.c. of **acetic acid,** and the test-tube containing the mixture is placed in a beaker of boiling water. In about ten minutes the osazone separates out in shining yellow crystals. To identify the sugar, the **osazone** may be filtered off, washed with water, and, after drying, its melting-point taken, or its decomposition products studied.

Dextrose (Glucose, Grape Sugar).

$CH_2(OH)(CH.OH)_4.CHO$

Dextrose crystallises with 1 mol. of water in odourless, colourless, warty masses. It is not so sweet as cane sugar. It is readily soluble in water or dilute alcohol, only with difficulty in strong alcohol, crystallising from it in the anhydrous state ; it is also insoluble in ether. Its solution rotates the plane of rays of polarised light to the right (*i.e.*, it is *dextro-rotatory*). $[\alpha]_D = +52 \cdot 7°$.

1. When heated in a dry tube, ordinary dextrose melts at 80-86°, the anhydrous compound at 146°, becoming brown when more strongly heated, and giving off a smell resembling burnt sugar. The brown mass so obtained is soluble in water.

***2. Concentrated sulphuric acid** does not char dextrose in the cold (distinction from sucrose) ; charring only takes place after heating for some little time. If the dextrose is in solution the sulphuric acid must only be added a little at a time, and the mixture cooled between each addition, otherwise the heat generated by the mixing with the water may cause charring.

***3.** On heating with **sodium hydroxide** the solution becomes first yellow and then reddish-brown. If the mixture

is now acidified with dilute nitric acid, the colour changes to pale yellow, and a smell resembling that of burnt sugar is noticed. (Distinction from sucrose.)

4. On adding **lead acetate** to a solution of dextrose, boiling the mixture for a few seconds and adding **ammonium hydroxide** till a precipitate is just produced, and again boiling, the precipitate assumes a salmon-pink colour. (Distinction from sucrose and lactose.)

Reactions depending upon the Reducing Action of Dextrose.

***5.** Add a solution of dextrose to **Fehling's solution,** and boil: a yellow precipitate of cuprous hydroxide will be produced, which rapidly becomes converted into red **cuprous oxide** (Cu_2O).

***6.** On adding **silver nitrate,** then ammonium hydroxide, and placing the test-tube in a beaker of boiling water, reduction takes place, a silver mirror forming on the sides of the tube.

7. The crystallised osazone of dextrose melts at 210° (p. 311).

Sucrose (Saccharose, Cane Sugar).

$$C_{12}H_{22}O_{11}$$

Sucrose crystallises from water in hard four-sided prisms. It is readily soluble in water, sparingly so in alcohol. It melts at 160-161°, and on cooling does not at once become crystalline again. It loses water at 200-210°, and becomes converted into a brown mass (caramel), which is soluble in water. It is dextro-rotatory. $[\alpha]_D = +66{\cdot}5°$.

***1. Concentrated sulphuric acid** chars sucrose or its solutions in the cold, the mixture becoming brown and rapidly black. A strong solution, to which sulphuric acid has been

added, swells up; steam, carbon dioxide, and other gases being evolved.

***2.** When heated with sodium hydroxide, solutions of sucrose are not coloured brown, at the most a light straw colour is produced. On acidifying the alkaline solution with nitric acid, no smell of burnt sugar is noticeable. (*Cf.* Dextrose, § 3, p. 312.)

3. On heating a solution of sugar with **lead acetate,** and adding **ammonium hydroxide** until a precipitate is produced, then again heating, no change of colour takes place. (*Cf.* Dextrose and Lactose.)

***4.** It does *not* reduce an alkaline copper solution, or a solution of a silver salt. If, however, the sugar solution is first heated for some minutes with dilute sulphuric acid, it is converted into an equimolecular mixture of dextrose and lævulose, and will then reduce Fehling's solution.

$$C_{12}H_{22}O_{11} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Lævulose.}}{C_6H_{12}O_6}$$

The solution so obtained is called "invert sugar," and is lævo-rotatory, *i.e.* it rotates the plane of polarised light to the left. Dextrose and lævulose are stereo-isomers (see p. 259).

Sucrose does *not* form an **osazone,** but it may be recognised in presence of dextrose, lactose, and maltose, because it does not reduce Fehling's solution. In a mixture with these other sugars, its presence may be proved by heating the solution on a water bath with Fehling's solution until no more reduction takes place, *i.e.* till on further addition of a small quantity of Fehling's solution the blue colour remains. The precipitated cuprous oxide is then filtered off, the solution acidified with dilute hydrochloric acid, and boiled for about five minutes. It is now neutralised with sodium hydroxide and again heated with Fehling's solution: further reduction taking placc shows that sucrose was present, and has been inverted by boiling with hydrochloric acid.

Lactose (Milk Sugar).

$C_{12}H_{22}O_{11}$

Lactose forms large hard warty crystals, containing 1 mol. of water of crystallisation. As usually obtained it is a white sandy powder. It is not very sweet to the taste. It is fairly soluble in water, but insoluble in ether or absolute alcohol. It is dextro-rotatory. $[\alpha]_D = + 52{\cdot}53°$.

1. On heating lactose in a dry tube, it is converted into an amorphous brown mass, which is soluble in water.

2. **Concentrated sulphuric acid** has no action in the cold, but, on heating or on long standing in the cold, the mixture becomes yellow, then brown, and finally black, with evolution of carbon dioxide and sulphur dioxide.

*3. When lactose is heated with **caustic alkalis**, the solution becomes yellow, and then brownish-red. On acidifying this solution with dilute nitric acid, it becomes colourless, and a smell resembling that of burnt sugar is produced. (Distinction from sucrose.)

*4. On boiling a solution of lactose with **lead acetate** for a few seconds, then adding **ammonium hydroxide** until a white precipitate is produced (it should not be added in excess) and again boiling, the precipitate becomes cream coloured. (*Cf.* Dextrose and Sucrose.)

*5. **Fehling's solution** is reduced by lactose on warming.

6. The osazone of lactose melts and decomposes at 200°.

Maltose.

$C_{12}H_{22}O_{11}$

Maltose crystallises with 1 mol. of water in colourless needles, which are *very* soluble in water. It is almost insoluble in absolute alcohol. It is strongly dextro-rotatory.

$$[\alpha]_D = + 136{\cdot}8°$$

1. When moistened with a drop of water, and gently warmed with concentrated **sulphuric acid,** maltose chars. In the cold, charring does not take place.

***2.** On boiling with caustic alkalis, the solution first turns yellow, then brown. If the brown solution is acidified with dilute **nitric acid** the colour is destroyed, and an odour of burnt sugar is produced.

***3. Fehling's solution** is reduced when boiled with maltose.

***4.** When maltose is boiled for a few seconds with a solution of **lead acetate,** then **ammonium hydroxide** added till a precipitate is just produced, and again boiled, the white precipitate first formed assumes a pinkish tinge.

***5.** The osazone of maltose melts at 205°.

Maltose can be detected in presence of dextrose, by forming the osazones; the mixed osazones are then boiled with a small quantity of water and rapidly filtered. On cooling the maltosazone crystallises out from the filtrate; the dextrosazone is insoluble in water.

SYNOPTIC TABLE SHOWING BEHAVIOUR OF SUGARS WITH VARIOUS REAGENTS.

Reagent.	Dextrose.	Sucrose.	Lactose.	Maltose.
1. Concentrated sulphuric acid	No action in the cold, chars on heating.	Chars in the cold.	Chars on heating.	Chars on heating.
2. Sodium hydroxide solution on boiling.	Turns brown. On adding nitric acid, smell of burnt sugar.	No change.	Turns brown. On adding nitric acid, smell of burnt sugar.	Turns brown. On adding nitric acid, smell of burnt sugar.
3. Fehling's solution.	Reduction on boiling.	No reduction.	Reduction on boiling.	Reduction on boiling.
4. Lead acetate and ammonium hydrate.	Salmon - pink precipitate.	White precipitate.	Very light yellowish - pink precipitate.	Very light yellowish - pink precipitate.
5. Phenylhydrazine.	Dextrosazone, yellow crystals, m.p. 210°.	—	Lactosazone, yellow crystals, m.p. 200°.	Maltosazone, yellow crystals, m.p. 205°.

Starch (Amylum).

$(C_6H_{10}O_5)_n$

Starch is a white powder, the structure of which, when examined under the microscope, is seen to consist of characteristic concentrically-striated granules, which vary in size, shape and general appearance according to its origin. It is insoluble in cold water; when heated, the granules burst, the cell wall remaining insoluble, but the granulose contained within the cell dissolves, forming a gelatinous mucilage, called **starch paste.**

1. When heated in a dry tube, starch chars, water and combustible gases are given off, and an unpleasant odour resembling burnt leather is noticed.

2. On heating with concentrated **sulphuric acid,** starch quickly chars, sulphur dioxide and carbon dioxide being evolved.

3. When starch is boiled with **dilute sulphuric acid** it is converted into dextrin, and then into dextrose.

$$(C_6H_{10}O_5)_n + nH_2O = \underset{\text{Dextrose}}{n(C_6H_{12}O_6)}$$

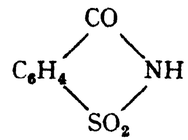
If the mixture has only been boiled for a short time, the **dextrin** is sure to be present with the **dextrose,** and on the addition of **iodine** it produces a red colour.

*4. To a neutral solution of starch paste dissolved in a large quantity of water, add two or three drops of **iodine solution**: a deep blue coloration of **iodide of starch** is produced. The colour disappears on addition of sodium thiosulphate or on boiling, returning again on cooling. (See p. 146.)

5. **Tannic acid** produces a precipitate with starch solution.

Starch may be separated from mixtures containing other substances, owing to its insolubility in cold water and other solvents. For example, water will remove most acids from it, and, if caustic alkali is added, aniline and other bases may be extracted from it by means of ether.

Saccharin (Glusidum, Gluside).



Saccharin, or benzoyl sulphone imide, is a white powder, with a very sweet taste. On heating, it fuses at 220°, and then sublimes with partial decomposition. It is only slightly soluble in cold water, but more so in hot water, but is easily soluble in alcohol or ether. Saccharin dissolves readily in ammonia and in sodium bicarbonate. Soluble saccharin is prepared by dissolving saccharin in a solution of sodium bicarbonate, and evaporating to dryness.

***1.** Place about 1 grm. of potassium hydroxide in a crucible, add 2 or 3 drops of water, and heat until fused. Now drop on to the fused mass about 0·2 of a grm. of saccharin, and continue the fusion for a minute or two, taking care not to char the mixture. Cool, and dissolve in water, acidify with dilute hydrochloric acid, and neutralise with ammonia. Now add a few drops of ferric chloride, when a violet-purple colour will be produced. This coloration is due to the presence of salicylic acid (see p. 264), which is produced when saccharin is fused with alkalis.

$$C_6H_4\left\langle{}^{CO}_{SO_2}\right\rangle NK + 3KOH = C_6H_4\left\langle{}^{COOK}_{OK}\right. + NH_3 + K_2SO_3$$

***2.** Saccharin dissolves in **sodium carbonate** with evolution of carbon dioxide. On acidifying the solution, and allowing to stand a few minutes, the saccharin crystallises out in lustrous plates.

3. Silver nitrate produces, from neutral solutions, a white precipitate of silver saccharate.

$$C_6H_4\left\langle{}^{CO}_{SO_2}\right\rangle NK + AgNO_3 = C_6H_4\left\langle{}^{CO}_{SO_2}\right\rangle NAg + KNO_3$$

*4. Place a little saccharin in a test-tube, cover it with aniline, and boil for about half a minute. On cooling, and allowing to stand a short time, crystals of the anilide separate out. These can be obtained free from aniline by washing with a little dilute hydrochloric acid. After recrystallising from dilute alcohol, the m.p. will be found to be 189°.

$$C_7H_5SO_3N + C_6H_5NH_2 = NH_2 . SO_2 . C_6H_4 . CO . NHC_6H_5$$

CHAPTER XVII.

BASES, GLUCOSIDES, ETC.

THIS chapter includes the important bases **aniline, pyridine,** and **quinoline,** the two latter substances being frequently produced when the alkaloids (Chap. XVIII.) are fused with caustic alkalis, or strongly heated with zinc dust. The reactions of the glucosides **salicin** and **digitalin,** and of the synthetic drugs **acetanilide, phenacetin,** and **antipyrin,** some of which are very similar to those of the alkaloids, are also given here. **Urea,** owing to its basic character, is also placed in this chapter.

Aniline (Aminobenzene).

$$C_6H_5NH_2$$

Aniline is a colourless liquid, b.p. 182·5°, having a peculiar characteristic odour. It is readily volatile with steam, but very slightly soluble in water; it is, however, readily soluble in alcohol or ether. Aniline rapidly turns brown on standing, but becomes colourless again on being redistilled. It forms crystalline salts with acids. They are decomposed, with regeneration of aniline, by caustic alkalis, but not by ammonia

(*a*) $C_6H_5NH_2 + HCl = C_6H_5NH_2 . HCl$

(*b*) $C_6H_5NH_2 . HCl + KOH = C_6H_5NH_2 + KCl + H_2O$

***1. Bleaching powder solution,** when added to a dilute solution of aniline or its salts, produces a purple-violet coloration, which becomes green on standing. If this solution is

diluted with water until it is practically colourless, and then a drop or two of **dilute ammonium sulphide** added, an intense rose-red coloration is formed; the colour, however, rapidly disappears. This reaction is extremely delicate, often showing when the addition of bleaching powder solution gives no blue coloration.

***2. Diazo Reaction.**—To a cold solution of aniline in dilute hydrochloric acid add six to eight drops of a dilute solution of **potassium** or **sodium nitrite,** keeping the mixture cool by holding under the tap. Now add a few drops of a solution of α or β **naphthol** dissolved in sodium hydroxide, when a brilliant scarlet coloration will be produced (it may be necessary to add more alkali). This coloration is due to formation of **benzene-azo-naphthol,** and is shown by all primary aromatic amino compounds. The course of the reaction is as follows: The aniline hydrochloride is first converted into **diazobenzene chloride,** and this, on the addition of the α or β naphthol, forms benzene-azo-naphthol.

$$(a)\quad C_6H_5NH_2 . HCl + HO . NO = C_6H_5N : N . Cl + 2H_2O$$

$$(b)\quad C_6H_5N : N . Cl + C_{10}H_7 . OH = C_6H_5N : N . C_{10}H_6 . OH + HCl$$

Diazo reactions are also used as tests for nitrites (§ 7, p. 164) and for phenols (§ 5, p. 267).

***3. Carbylamine Reaction.**—When a drop or two of aniline is mixed with an alcoholic solution of sodium or potassium hydroxide, then a few drops of chloroform added and the mixture warmed, a most disagreeable smell of **phenylisonitrile** or **carbylamine** is produced. (See p. 281.)

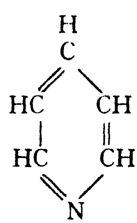
$$C_6H_5NH_2 + CHCl_3 + 3KOH = C_6H_5 . N \vdots C + 3H_2O + 3KCl$$

4. A solution of aniline in concentrated sulphuric acid gives a blue colour on addition of **potassium dichromate.**

In order to apply the tests for aniline, it should be separated from other substances with which it may be mixed. To do this, sodium hydroxide is added till the solution is strongly

alkaline, the alkaline solution is then extracted with ether, and, after evaporating off the ether, the various tests may be applied to the residue. The addition of alkali liberates aniline from its salts, and at the same time converts acids and phenols into salts, which are insoluble in ether. If alkaloids are present, and it is desired to obtain a separation, the alkaline mixture should be steam distilled. The aniline passes over with the steam, and the alkaloids, etc., remain behind. A few alkaloids, such as nicotine and coniine, and such bases as pyridine and quinoline, are both soluble in ether and volatile with steam, but their presence would not materially interfere with the reactions of aniline.

Pyridine.



Pyridine is obtained from bone oil, and, when pure, is a colourless liquid, having a penetrating and characteristic smell; it boils at 116°. It is soluble in water, alcohol, or ether in all proportions. Pyridine is a powerful base, forming salts with acids, most of which are soluble in water, but the sulphate is sparingly soluble. Pyridine fumes in presence of volatile acids, and sodium hydroxide liberates it from its salts.

(*a*) $C_5H_5N + HCl = C_5H_5N . HCl$

(*b*) $C_5H_5N . HCl + KOH = C_5H_5N + KCl + H_2O$

1. The aqueous solution of pyridine has an alkaline reaction, and precipitates the hydroxides of most metals from solutions of their salts, *e.g.* **iron, cobalt.**

*2. **Hydrogen platinichloride** gives with solutions of pyridine in hydrochloric acid an orange-yellow crystalline precipitate of pyridihe platinichloride.

$$2C_5H_5N + H_2PtCl_6 = (C_5H_5N)_2, H_2PtCl_6$$

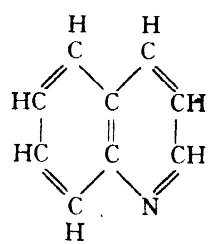
It is soluble in hot water, but is reprecipitated on boiling as an almost insoluble light yellow salt, having the formula $(C_5H_5N)_2PtCl_4$.

*3. On heating a few drops of pyridine in a test-tube with an equal quantity of methyl iodide, a vigorous reaction takes place. On now adding a small piece of solid caustic alkali, and again heating, a most offensive smell similar to that of highly rotten fish is produced.

4. The general reagents for alkaloids produce precipitates with pyridine (p. 334).

Pyridine may be separated from most substances by rendering the solution strongly alkaline with caustic alkali and steam distilling. From other volatile bases it may be separated by the action of fuming nitric or chromic acid, which decomposes them, while pyridine is not affected.

Quinoline.



Quinoline is found in bone oil and in coal tar. It is a colourless or slightly yellow mobile liquid, having a peculiar and characteristic aromatic smell. It boils at 238°, but even at ordinary temperatures it evaporates slowly. Quinoline is very slightly soluble in cold water, but is volatile with steam, and is readily soluble in most organic solvents. The basic

properties of quinoline are strongly marked, and its salts with acids are more or less deliquescent.

1. Concentrated **sulphuric acid** forms a white salt, which dissolves in excess of the acid, producing a colourless solution.

$$2C_9H_7N + H_2SO_4 = (C_9H_7N)_2, H_2SO_4$$

2. When solutions of the salts of **iron, aluminium, zinc,** etc., are shaken with a little quinoline, the hydroxides of the metals are precipitated.

***3. Hydrogen platinichloride** gives with a solution in hydrochloric acid a yellow precipitate of quinoline platinichloride, which is soluble in hot water.

$$2C_9H_7N + H_2PtCl_6 = (C_9H_7N)_2H_2PtCl_6$$

***4. Potassium dichromate,** when added to an acid solution of quinoline, produces, especially on shaking, a fine yellow crystalline precipitate of the dichromate.

$$2C_9H_7N \,.\, HCl + K_2Cr_2O_7 = (C_9H_7N)_2, H_2Cr_2O_7 + 2KCl$$

The dichromate is readily soluble in warm water, but crystallises out again on cooling.

5. The general reagents for alkaloids (p. 334) produce precipitates with quinoline. (Tannic acid, however, gives no precipitate.)

Quinoline may be separated from pyridine by means of **potassium dichromate** in acid solution, pyridine not producing a precipitate under these circumstances. Quinoline is very sparingly soluble in water, whereas pyridine is readily soluble.

Urea (Carbamide).

$$CO\begin{matrix} \diagup NH_2 \\ \diagdown NH_2 \end{matrix}$$

Urea forms colourless crystals; m.p. 132°. It is readily soluble in water or alcohol, but almost insoluble in ether.

***1.** When urea is gently heated just above its melting-point for a few minutes, it is converted into **biuret** and ammonia, a white sublimate being formed at the same time.

$$2NH_2 . CO . NH_2 = NH_2 . CO . NH . CO . NH_2 + NH_3$$

On dissolving the opaque residue in water, adding a few drops of caustic alkali, and then a drop or two of copper sulphate solution, a violet coloration is produced. (**Biuret reaction.**) When urea is more strongly heated it is converted chiefly into **cyanuric acid,** which remains as a white residue.

$$3NH_2 . CO . NH_2 = H_3C_3N_3O_3 + 3NH_3$$

If the cyanuric acid is boiled with water until it is partially dissolved (it is not readily soluble in water), and if to the solution one or two drops of dilute ammonia are added, then two or three drops of copper sulphate solution, an amethyst-coloured precipitate is produced.

***2.** Strong **nitric acid** produces from fairly strong solutions of urea a characteristic crystalline precipitate of **urea nitrate,** which is practically insoluble in nitric acid.

***3. Oxalic acid** gives with concentrated aqueous solutions of urea a crystalline precipitate of **urea oxalate.** Oxalate of urea may be produced from fairly small quantities of urea by dissolving it in amyl alcohol, instead of in water; the oxalic acid also being dissolved in this solvent. On mixing the cold solutions, a white crystalline precipitate is almost immediately obtained.

***4.** When **potassium** or **sodium nitrite** is added to a solution of urea which has been acidified with dilute sulphuric acid, the urea is decomposed with evolution of nitrogen and carbon dioxide.

$$NH_2 . CO . NH_2 + 2HO . NO = CO_2 + 2N_2 + 3H_2O$$

5. On heating with dilute mineral acids, urea is decomposed into **carbon dioxide** and an ammonium salt.

$$NH_2 . CO . NH_2 + H_2O + 2HCl = CO_2 + 2NH_4Cl$$

6. A 10 per cent. solution of **xanthydrol** in methyl alcohol gives a precipitate (dixanthyl urea) when added to a solution of urea in acetic acid. This method is used to detect and determine urea in urine.

Urea may be separated from mixtures of organic material by first extracting the solution (which has been made alkaline with caustic alkali) with ether. This will remove bases, most alkaloids, and oily or resinous products. Then evaporate to dryness, and extract with warm absolute alcohol or, better, amyl alcohol: this will dissolve the urea, but not salts of acids, and only to a very limited extent, sugars. The urea may be obtained from the alcoholic solution by evaporating to dryness, or, better, if amyl alcohol has been employed, by adding a cold solution of oxalic acid in the same solvent, when urea oxalate will be precipitated.

Acetanilide (Antifebrin).

$$C_6H_5 . NH . COCH_3$$

Acetanilide forms colourless, odourless shining plates; m.p. 113°. It is readily soluble in alcohol, ether, chloroform, or hot water.

***1.** To a little acetanilide, which has been placed in a porcelain basin, add a few drops of concentrated **sulphuric acid**, and sprinkle a small quantity of powdered **potassium dichromate** on it; a red coloration will be produced, which rapidly becomes dull green. Red streaks, however, reappear on rubbing the grains of dichromate with a glass rod.

***2.** When acetanilide is heated with caustic alkali, it decomposes, forming an alkali acetate and aniline.

$$C_6H_5NH . CO . CH_3 + KOH = C_6H_5NH_2 + CH_3COOK$$

The aniline may be recognised by dissolving in a little alcohol and applying the **carbylamine** reaction (p. 321).

3. On heating acetanilide with about 1 c.c. of concentrated hydrochloric acid for about one minute, aniline and acetic acid are produced.

$$C_6H_5NHCOCH_3 + H_2O = C_6H_5NH_2 + CH_3COOH$$

The solution may be tested for aniline and acetic acid.

4. When a little acetanilide is heated with concentrated sulphuric acid and alcohol, the characteristic fruity odour of ethyl acetate is produced. The sulphuric acid first decomposes the acetanilide into aniline and acetic acid; the alcohol then reacts with the acetic acid, producing ethyl acetate.

***5.** On boiling with **ferric chloride,** a turbidity is produced, but no red coloration, although the colour of the ferric chloride becomes darker. (Distinction from antipyrin and phenacetin.)

6. Place a mixture of acetanilide with about double its weight of **sodium nitrite** in an evaporating basin, and moisten with concentrated **hydrochloric acid**: a yellow coloration will be produced, which, when heated on a water bath, turns green, and, on evaporating to dryness, red.

***7.** To a little acetanilide, contained in an evaporating basin, add two or three drops of **mercurous nitrate**: on evaporating just to dryness a green mass will be obtained, which becomes a brilliant blood-red when moistened with concentrated sulphuric acid.

8. Mandelin's reagent (p. 372) produces an orange-red coloration, which changes to red, and finally to grey.

Phenacetin (para-**Acetamido-ethoxybenzene**).

$$C_2H_5O \,.\, C_6H_4 \,.\, NH \,.\, COCH_3$$

Phenacetin forms colourless, odourless crystalline leaflets; m.p. 135°. It is easily soluble in ether or chloroform, moderately soluble in hot, and almost insoluble in cold water.

1. On heating with concentrated **sulphuric acid** and **alcohol,** an odour of **ethyl acetate** is produced.

***2.** When heated with equal volumes of concentrated nitric acid and water, a yellow or orange coloration is produced, and if the quantity taken is not too small, yellow crystals separate on cooling. If caustic alkali is added in excess to the mixture, a red coloration is produced, which is intensified on boiling.

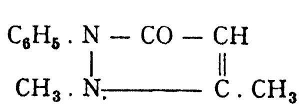
3. Mandelin's reagent (p. 372) produces a very pale blue coloration.

***4.** Mix a small quantity of phenacetin with two or three times its bulk of **zinc dust,** and heat till it chars. Cool, and then boil with 2 or 3 c.c. of water; filter, and add **ferric chloride** to the filtrate. A deep violet coloration will be produced, owing to the formation of **salicylic acid** by the action of the zinc dust on the phenacetin.

***5.** On grinding up equal quantities of phenacetin and a **nitrite** in an evaporating dish, adding a drop or two of concentrated **sulphuric acid,** and then gently warming on a water bath, a green coloration, which changes to drab, is produced. (*Cf.* § 6, p. 327.)

6. On adding a few drops of concentrated **sulphuric acid** to phenacetin in a porcelain basin, and sprinkling a little powdered **potassium dichromate** on it, and allowing it to stand some time, a green coloration is produced.

Antipyrin (Phenazone, 1, Phenyl, 2, 3, dimethyl-pyrazolone).



Antipyrin forms colourless and odourless crystals, having a bitter taste; m.p. 114°. It is soluble in water or alcohol, but sparingly soluble in ether. Antipyrin, though basic in that it forms salts with acids, has no alkaline reaction. Antipyrin is much used in medicine as an antipyretic.

1. Antipyrin dissolves in warm concentrated **sulphuric acid,** forming a colourless solution.

***2.** When warmed with concentrated **nitric acid,** antipyrin colours it first yellow and then a deep red.

***3. Mandelin's reagent** (p. 372) produces a pale blue coloration, which gradually fades away.

***4. Mercurous nitrate,** when added in excess to a solution of antipyrin, produces a dirty green or yellow precipitate, which, on boiling, turns a deep red, and a red powdery precipitate gradually settles down.

***5.** To a solution of antipyrin add a small fragment of **sodium** or **potassium nitrite,** and then a few drops of dilute **sulphuric acid,** when a bright green coloration will be produced. The coloration is due to formation of **isonitroso-antipyrin.** If the solution is not too dilute, the isonitroso compound crystallises out in small green needles.

6. Sulphuric acid and **potassium dichromate** produce a green coloration, as with phenacetin. (See p. 328, § 6.)

7. Most of the general alkaloid reagents produce a precipitate with antipyrin (p. 334).

Sulphonal (Dimethyl-methane-diethylsulphone).

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} > C < \begin{matrix} SO_2 . C_2H_5 \\ SO_2 . C_2H_5 \end{matrix}$$

Sulphonal forms colourless prisms; m.p. 126°. It is slightly soluble in cold water or alcohol, rather more so in hot water (1 : 15), and readily in boiling alcohol; fairly soluble in chloroform and benzene. Sulphonal is used in medicine as a sedative.

1. When heated upon a piece of porcelain or platinum foil, sulphonal burns with a luminous flame, and evolves sulphurous anhydride. It leaves no residue.

***2.** Place a small quantity of powdered sulphonal in a test-tube, and cover it with powdered **potassium cyanide.**

On now fusing, noxious-smelling vapours of **mercaptan**, C_2H_5SH, are evolved.

(i) A piece of filter paper soaked in lead acetate is stained brown or black when held in the mouth of the test-tube.

(ii) Allow to cool, dissolve the fused mass in a little water, and acidify with hydrochloric acid. On now adding ferric chloride to this solution the blood-red coloration of ferric thiocyanate is produced.

***3.** When a little powdered sulphonal is mixed with **manganese dioxide**, and the mixture gently fused, mercaptan is evolved, and on lixiviating the melt with water, filtering from suspended manganese dioxide, then acidifying with hydrochloric acid, and adding barium chloride, a white precipitate of barium sulphate is produced.

Glucosides.

Glucosides are bitter substances of vegetable origin which, on being hydrolysed with acids or alkalis, yield a sugar (generally dextrose), and one or more other substances, the latter generally being phenols or aldehydes of the aromatic series. Thus on hydrolysis **salicin** yields **saligenin** (ortho-hydroxy-benzyl alcohol) and **dextrose**, while **amygdalin** gives **hydrocyanic acid, benzaldehyde**, and **glucose**; **digitalin** being split up into **glucose, digitalose**, and **digitaligenin**.

Salicin.

$C_{13}H_{18}O_7$

Salicin occurs in the bark of the willow. It forms silky needles, m.p. 201°, has a bitter taste, and is not readily soluble in water or cold alcohol, but is more readily so on boiling. It is insoluble in ether, but readily soluble in caustic alkali or glacial acetic acid.

1. When heated in a dry tube, salicin chars, and vapours are given off, which possess a smell rather resembling that of burnt sugar.

*2. If a small quantity of the solid substance is placed upon a white porcelain basin, and moistened with a drop of concentrated **sulphuric acid**, a blood-red coloration is produced.

3. On warming a solution of salicin with a solution of **silver nitrate** to which excess of ammonium hydroxide and a little caustic alkali has been added, the silver is reduced with formation of a mirror.

*4. On heating with **dilute sulphuric acid**, salicin is hydrolysed, **dextrose** and **saligenin** (orthohydroxy-benzyl alcohol) being produced.

$$C_{13}H_{18}O_7 + H_2O = C_6H_4\left\langle\begin{matrix} CH_2OH \\ OH \end{matrix}\right. + C_6H_{12}O_6$$

On making the hydrolysed solution alkaline, the dextrose reduces **Fehling's solution** on warming.

Further, on addition of a few drops of **potassium dichromate** to the acid mixture, the suspended saligenin becomes coloured pink. Finally, if about 1 grm. of powdered **potassium dichromate** is added to the hydrolysed mixture, and about a quarter of its volume of concentrated **sulphuric acid**, and the mixture then distilled from a small fractionating flask into a few cubic centimetres of water, **salicylic aldehyde** will be obtained, which may be recognised by its smell—odour of meadow-sweet,—and also by addition of a few drops of **ferric chloride**, which will produce a violet coloration.

5. **Mandelin's reagent** (p. 372) produces a purple-red coloration.

6. **Froehde's reagent** (p. 372), when added to a trace of salicin on a porcelain plate, gives a violet coloration.

7. **Erdmann's reagent** (p. 371) gives a bright red, the edges of the drop gradually becoming purple.

Digitalin.

$C_{29}H_{46}O_{12}$

Digitalin occurs in the seeds of the purple foxglove. When pure, it forms a white amorphous powder, and melts and decomposes at about 217°. It is readily soluble in water, sparingly soluble in cold alcohol, but readily in hot absolute alcohol. It is very slightly soluble in chloroform or ether. On saponification, digitalin is converted into digitaligenin, digitalose, and dextrose.

$$C_{29}H_{46}O_{12} + H_2O = \underset{\text{Digitaligenin}}{C_{18}H_{22}O_2} + \underset{\text{Digitalose}}{C_7H_{14}O_5} + \underset{\text{Dextrose}}{C_6H_{12}O_6}$$

1. Cold concentrated **sulphuric acid** turns digitalin, first golden-yellow, then brown, and, finally, after some time, red.

2. Cold concentrated **sulphuric acid** and a trace of powdered **potassium dichromate** produces a brown coloration, which gradually turns green.

***3.** On dissolving a small trace of digitalin in concentrated **sulphuric acid,** and stirring it with a glass rod moistened with **bromine water,** a mahogany-brown coloration is produced.

4. On warming a solution of digitalin with a solution of **silver nitrate,** to which excess of ammonium hydroxide and a little caustic alkali has been added, the silver is reduced, and a mirror formed.

5. Mandelin's reagent (p. 372) produces a mahogany-brown colour, which turns a deep cherry-red.

6. Froehde's reagent (p. 372) gives a brown colour, which changes to cherry-red, the edges gradually becoming grey.

7. Erdmann's reagent (p. 371) produces a brown coloration.

CHAPTER XVIII.

ALKALOIDS.

Most of the vegetable alkaloids are obtained from the family of the *Dicotyledons;* colchicin, indeed, is found in a *Monocotyledon.* But no alkaloids have been found in the great families of the *Compositæ* or of the *Labiatæ.* They usually occur in the plants combined with organic acids, such as citric, malic, and tannic acids. Owing to the remarkable physiological action of many of the alkaloids, they are very much employed in medicine. The majority of the alkaloids are extremely poisonous, and have a very bitter taste.

Most of the alkaloids are colourless, odourless, crystalline solids, which contain carbon, hydrogen, nitrogen, and oxygen. There are a few, however, containing no oxygen, which are liquids with unpleasant characteristic smells. **Nicotine, coniine,** and **sparteine** are examples of the latter class.

With very few exceptions, the alkaloids are practically insoluble in water. They are, however, soluble in absolute alcohol, benzene, chloroform, or amyl alcohol, also (with the exception of **morphine** and **narceine**) in ether. The solubility of the alkaloids in various solvents is made use of in separating them.

The alkaloids are bases, usually tertiary or secondary amines. They form, as a rule, well-defined crystalline salts with acids. In some cases, however, the basic character is only very feebly marked, the salts being decomposed by excess of water (hydrolysed). The salts are usually readily soluble in water, but not in ether, benzene, chloroform, etc. Generally, the alkaloids, owing to their insolubility in water,

are precipitated from the solutions of their salts by addition of caustic alkali; occasionally, the alkaloid is redissolved by excess of the precipitant. This is the case with morphine, which is dissolved almost as quickly as it is precipitated.

The following **general reagents** (see p. 371) precipitate most alkaloids :—

1. **Tannic acid**—white or yellowish-white precipitate.
2. **Picric acid**—yellow, generally crystalline, precipitate.
3. **Mercuric chloride**—white to yellow precipitate.
4. **Potassium-bismuth-iodide** (Dragendorff's reagent)—orange-red precipitate.
5. **Iodine in potassium iodide**—brown precipitate.
6. **Potassium mercury-iodide** (Mayer's reagent)—white to yellowish-white precipitate.
7. **Phosphomolybdic acid**—light yellow to brownish-yellow precipitate.

Special Reagents.—Besides giving precipitates with the **general reagents,** most of the alkaloids give "characteristic" reactions with special reagents. (See p. 371.) As a rule, these reactions are well marked and exceedingly delicate. They are best carried out as drop reactions (see p. 30), unless other directions are given.

OPIUM ALKALOIDS (MORPHINE, APOMORPHINE, CODEINE, NARCOTINE).

Morphine.

$C_{17}H_{19}NO_3$

Morphine occurs in opium as morphine meconate. (*Cf.* Meconic Acid, p. 270.) It crystallises in transparent, colourless prisms, containing 1 mol. H_2O, m.p. 230°, with decomposition. It is nearly insoluble in cold water, slightly soluble in boiling water (1 part in 160 parts); the solution has an alkaline

reaction. Morphine is almost *insoluble* in ether, chloroform, benzene, or alcohol. Hot amyl alcohol is the best solvent (1 part in 50 parts). The salts of morphine are readily soluble in water or alcohol. Morphine is precipitated from solutions of its salts by **caustic alkali,** but immediately dissolves in excess. **Ammonium hydroxide** only dissolves morphine slightly, therefore it is the best precipitant.

1. Concentrated sulphuric acid produces a pale rose-red coloration, changing to reddish-yellow. On heating, it becomes violet, and, finally, brown. The addition of powdered **potassium dichromate** changes the colour to greenish-brown.

***2.** On intimately mixing in a mortar a little morphine with three or four times its bulk of **sucrose,** placing the mixture on a white tile, and adding a drop of concentrated **sulphuric acid,** a deep-red coloration is produced (apomorphine produces no coloration).

***3.** When a little morphine is dissolved in a small quantity of concentrated **sulphuric acid** contained in an evaporating dish, and a trace of an **arsenate** added, a deep bluish-green coloration is produced on warming.

***4.** To a small quantity of morphine in an evaporating dish add a few drops of concentrated **sulphuric acid** and a small crystal of **ferrous sulphate,** heat on the water bath for one minute, and stir in the crystal. Cool, and add excess of ammonium hydroxide to the pink solution, when a rich red, rapidly becoming bright violet, is formed. (Distinction from codeine.)

5. Concentrated **nitric acid** produces an orange-red coloration, which changes to yellow on heating.

6. Froehde's reagent gives a purple coloration, which becomes green, and finally, brownish-yellow.

7. Mandelin's reagent produces a brownish-purple coloration, which gradually becomes grey.

***8.** When a drop of **ferric chloride** is added to a small quantity of morphine, a bluish-green coloration is formed. On now adding a drop of **potassium ferricyanide,** and stirring

with a glass rod, a deep blue precipitate of Turnbull's blue is obtained.

***9.** On addition of a solution of morphine to **iodic acid, iodine** is liberated ; if the solution is very dilute, the presence of the liberated iodine can be readily detected by means of starch paste.

***10.** When morphine is moistened with **formaldehyde,** and then with two to three drops of concentrated **sulphuric acid,** an intense purple-red colour, changing to violet-blue, is obtained.

Apomorphine.

$C_{17}H_{17}NO_2$

Apomorphine is a snow-white amorphous substance, readily soluble in alcohol, ether, chloroform, or benzene ; m.p. 295-300°.

1. Solutions of apomorphine rapidly acquire a green tinge, and finally become brown. With solutions of the **salts** of **apomorphine** these colour changes are shown after addition of alkali.

2. On adding a drop of concentrated **sulphuric acid,** and then sprinkling with **potassium dichromate,** an olive-green, changing to brown-green, is produced.

***3. Nitric acid** produces a purple-red coloration, becoming mahogany-brown.

4. Froehde's reagent gives a deep green coloration which gradually assumes a bluish tinge.

5. Mandelin's reagent produces a greyish or greenish-blue coloration.

***6. Ferric chloride** gives a red or purple-red coloration, becoming brownish-black on heating (distinction from codeine).

Codeine (Methyl Morphine).

$C_{17}H_{17}NO(OCH_3)OH$

Codeine crystallises from water in well-defined orthorhombic prisms, containing 1 mol. H_2O. Anhydrous codeine melts at 155°. It is readily soluble in alcohol, amyl alcohol, ether, chloroform, or benzene; fairly soluble in hot water. It is a strong base, with an alkaline reaction. Its salts are readily soluble in water.

***1.** Grind a little codeine in a mortar with about three times its bulk of **sugar,** and moisten the mixture with concentrated **sulphuric acid**; a light red colour, which slowly changes to violet-purple, will be formed.

***2.** When a drop of concentrated **nitric acid** is added to a solution of codeine in concentrated **sulphuric acid,** a deep red coloration is produced.

3. Froehde's reagent produces a dirty green coloration, which becomes bright green, then blue, and, after standing some time, yellow.

4. Mandelin's reagent gives a greenish-grey to greyish-blue coloration.

***5.** On moistening a trace of codeine with **formaldehyde,** and then with two to three drops of concentrated **sulphuric acid,** a bluish-violet coloration is produced.

6. Addition of **sulphuric acid** followed by a crystal of **ferrous sulphate** produces a blue colour.

Narcotine.

$C_{22}H_{23}NO_7$

Narcotine crystallises from alcohol in colourless glittering prisms or groups of needles; m.p. 176°. It is soluble in alcohol, ether, or chloroform; almost insoluble in water. It is a

feeble base, its salts having an acid reaction, being more or less hydrolysed in aqueous solutions.

*1. Concentrated **sulphuric acid,** when added to a trace of narcotine in an evaporating basin, produces a greenish-yellow coloration, which on heating on the water bath, becomes a deep brownish-red, changing to a dirty violet. **Potassium dichromate** added to a solution of narcotine in concentrated sulphuric acid, produces a fine brown coloration.

*2. If a little narcotine is warmed with concentrated **sulphuric acid** in an evaporating dish, and a drop of **ferric chloride** added, the brownish-red coloration at first produced becomes an intense crimson.

*3. When a little narcotine is ground up with about four times its bulk of **sugar,** and the mixture moistened with concentrated **sulphuric acid,** a mahogany-brown coloration is produced.

4. **Nitric acid** gives a yellow to orange coloration.

5. On heating a solution of narcotine in dilute **hydrochloric acid** with **bromine water,** a yellow precipitate is produced, which dissolves on boiling. By carefully adding bromine water drop by drop to the hydrochloric acid solution, and boiling, a rose-red coloration is formed, which is destroyed by adding excess of bromine water.

6. **Erdmann's reagent** produces an orange-yellow coloration, which momentarily turns pink, then yellow again.

7. **Froehde's reagent** forms a deep grass-green coloration.

8. **Mandelin's reagent** gives an orange coloration, which gradually becomes pink.

CINCHONA ALKALOIDS.

The cinchona alkaloids all have well-marked basic properties, some of them displacing ammonia from its compounds. The free alkaloids are generally readily soluble in ether or chloroform. The solutions of the sulphates of some of the cinchona alkaloids show a strong blue fluorescence. The

cinchona alkaloids dealt with here are quinine, quinidine, and cinchonine.

Quinine.

$C_{20}H_{24}N_2O_2, 3H_2O$

Free quinine usually has the appearance of an amorphous or resinous mass. In commerce it is generally obtained as a coarse powder with a brownish-yellow tint. It may, however, be obtained crystalline from its solution in alcohol; m.p. 175°. On evaporating an ethereal solution, it separates as a gelatinous mass. Quinine is only sparingly soluble in water, but more readily in ammonium hydrate. It is readily soluble in petroleum spirit and benzene. It is strongly basic, its solution turning red litmus blue.

1. Concentrated **sulphuric acid,** added to a little quinine, dissolves it, forming a colourless solution, which on addition of a crystal of **potassium dichromate,** becomes grass-green.

***2.** Solutions of quinine in dilute sulphuric acid exhibit a strong blue fluorescence. The fluorescence shows best in dilute solutions, to which has been added a large excess of dilute sulphuric acid, and may be best seen by looking down into a test-tube held over a piece of black paper.

***3. Ammonium oxalate,** added to a solution of quinine sulphate, produces a white crystalline precipitate. Precipitation is accelerated by shaking. (Distinction from quinidine.)

***4.** Dissolve a little quinine sulphate in **acetic acid,** add an equal bulk of alcohol, and then an **alcoholic** solution of iodnie. On now warming and allowing to stand a few minutes, a black crystalline powder of **iodoquinine** separates out, which possesses a very characteristic golden lustre.

***5. Thalleoquinine Reaction.**—Make a dilute solution of bromine in water,† and add about 1 c.c. of this solution to about 10 c.c. of a solution of quinine sulphate, and then two

† A freshly prepared solution of chlorine water may be used instead of the bromine water.

or three drops of ammonia, when a bright green precipitate or coloration will be produced (thalleoquinine). On adding to this a few drops of a freshly prepared solution of **potassium ferricyanide,** the colour changes to a brilliant red (roseoquinine).

6. If a small quantity of quinine is placed in an evaporating dish, moistened with a few drops of concentrated hydrochloric acid, and evaporated to dryness over a naked flame, just before it chars it turns a violet colour, and if the heating is continued violet vapours, resembling those of iodine, are given off. *This reaction is peculiar to the quinine alkaloids.*

***7. Mandelin's reagent** gives no coloration, but, on addition of a drop of nitric acid, a violet coloration is obtained.

Quinidine.

$C_{20}H_{24}N_2O_2$

Quinidine is deposited from alcohol in monoclinic efflorescent prisms or needles, with 2 mols. H_2O. The anhydrous substance melts at 170°, first becoming brown. It is soluble in water, and fairly soluble in ether or alcohol.

1. Concentrated **sulphuric acid,** when added to a trace of quinidine on a white plate, dissolves it without coloration, but on adding a crystal of **potassium dichromate,** it turns a grass-green.

***2.** A solution of **potassium iodide** gives a heavy sandy precipitate with solutions of quinidine.

***3.** Quinidine gives the **thalleoquinine** reaction. (*Cf.* Quinine, § 5.)

4. If a small quantity of quinidine is placed in an evaporating dish moistened with a few drops of concentrated hydrochloric acid, and evaporated to dryness over a naked flame, just before it chars it turns a violet colour, and, if the heating is continued, violet vapours resembling those of iodine are given off.

***5. Mandelin's reagent** produces no coloration, but on addition of a drop of **nitric acid** to the mixture, a violet coloration appears.

Cinchonine.

$C_{19}H_{22}N_2O$

Cinchonine crystallises in white shining anhydrous prisms. It melts at 255°. forming a colourless liquid, and at a higher temperature partially sublimes. It is almost insoluble in cold water, and only very slightly in boiling water. It is fairly soluble in boiling alcohol, but much more readily in amyl alcohol, and dissolves most easily in a mixture of six parts chloroform and one part alcohol; it does not fluoresce. Solutions of cinchonine have an alkaline reaction. Its salts are fairly soluble in water or alcohol.

1. When carefully heated in a dry tube, cinchonine first melts, then gives off white fumes, which condense on the cold sides of the test-tube in small needles.

2. On adding a little powdered **potassium dichromate** to a solution of cinchonine in concentrated **sulphuric acid,** a grass-green coloration is produced.

3. On adding **chlorine water** to a solution of a salt of cinchonine, no change is produced, but on addition of **ammonia,** a yellowish-white precipitate is formed. (*Cf.* Quinine and Quinidine.)

***4. Potassium ferrocyanide,** when added to a solution of a salt of cinchonine, produces a light yellow flocculent precipitate of **cinchonine ferrocyanide**; if excess of the precipitant is added, and the mixture cautiously warmed, the precipitate dissolves, separating out again, on cooling, in golden-yellow crystals. (Characteristic reaction.)

5. Cinchonine when evaporated to dryness with a few drops of concentrated hydrochloric acid gives the same reaction as quinine and quinidine.

*6. **Mandelin's reagent** gives no coloration with cinchonine, but on adding a drop of **nitric acid** to the mixture, a violet coloration is formed.

Cocaine (Benzoyl-methyl-ecgonine).

$C_{17}H_{21}NO_4$

Cocaine is the characteristic alkaloid of the coca leaves. It forms colourless prisms; m.p. 97-98°, subliming at higher temperatures with partial decomposition. It is very slightly soluble in water, but dissolves readily in alcohol, ether, chloroform, benzene, or petroleum spirit. Cocaine is a very strong base, and its salts are readily soluble in water. Cocaine is used in surgery as a local anæsthetic. When the smallest trace of a 4 per cent. solution of the hydrochloride is placed on the tongue, it produces a peculiar numb feeling. (See footnote, p. 346.)

1. **Sulphuric acid** produces no coloration, but on addition of a little powdered **potassium dichromate,** a dirty brown coloration is obtained.

*2. On boiling cocaine with concentrated **sulphuric acid** and a few drops of alcohol, the fragrant and characteristic odour of **ethyl benzoate** is produced. When heated with acids, cocaine is split up into benzoic acid, methyl alcohol, and ecgonine.

*3. When **potassium permanganate** is added to a moderately strong solution of cocaine, a purple precipitate of **cocaine permanganate** is produced.

*4. Add **potassium chromate** to a solution of cocaine, and then two or three drops of concentrated **hydrochloric acid**; a yellow precipitate will be obtained. Many alkaloids give a precipitate with potassium chromate in neutral solutions, cocaine only after adding hydrochloric acid.

Strychnine.

$C_{21}H_{22}N_2O_2$

Strychnine occurs together with brucine in the seeds and bark of *Strychnos Nux Vomica*, and in the *St. Ignatius Bean*. It forms colourless rhombic prisms, which have a strongly alkaline reaction, m.p. 267°. It is only slightly soluble in water, insoluble in alcohol or ether, sparingly soluble in dilute alcohol. It is, however, readily soluble in chloroform. The salts of strychnine are readily soluble in water or alcohol.

***1.** A drop of concentrated **sulphuric acid,** added to strychnine, produces no coloration, but on adding the smallest trace of powdered **potassium dichromate,** a blue or violet coloration is obtained.

***2.** Place a little strychnine on a watch glass, and cover it with a solution of **potassium dichromate,** and add a drop of nitric acid ; stir for a minute, and pour off the excess of potassium dichromate. Wash the residue on a watch glass by decantation with a small quantity of water, which should be carefully drained off. Now add to the strychnine chromate which remains on the watch glass a few drops of concentrated **sulphuric acid,** when the *violet* coloration already mentioned will be produced.

3. Concentrated **nitric acid** added to strychnine produces a slight yellow coloration, becoming darker on warming.

***4. Mandelin's reagent** gives a blue coloration rapidly changing to a brilliant violet. Addition of ammonia turns it rose-red. (Distinction in presence of other alkaloids.)

Brucine.

$C_{23}H_{26}N_2O_4, 4H_2O$

Brucine forms colourless transparent crystals, m.p. 178°, which are sparingly soluble in water, but readily soluble in

absolute alcohol, in warm amyl alcohol, and in chloroform; almost insoluble in ether. The salts of brucine are readily soluble in water.

***1.** Concentrated **sulphuric acid** produces a pale rose-red coloration, which slowly turns yellow. (Distinction from strychnine.) On adding a few grains of **potassium dichromate** a red-brown coloration is obtained.

***2.** On placing a little brucine in an evaporating dish, and moistening it with concentrated **nitric acid**, an intensely red coloration is produced, which subsequently becomes yellowish-red. On evaporation on a water bath, the colour becomes yellowish-brown. If it is heated long enough to get rid of the excess of nitric acid, and then a drop of **stannous chloride** added, the yellow changes to an intense violet. (*Cf.* Nitric Acid, p. 126.)

***3.** To a trace of powdered brucine, contained in an evaporating dish, add a few drops of a solution of **mercurous nitrate**: no change of colour will be produced; but on evaporating on the water bath, a red coloration is obtained, becoming violet at the edges of the drop.

4. Erdmann's reagent produces a bright yellow coloration, becoming an intense red.

5. Froehde's reagent produces a light red coloration, becoming a deep reddish-brown.

6. Mandelin's reagent gives a rose-red coloration quickly changing to orange.

Veratrine (Cevadine).

$$C_{32}H_{49}O_9N$$

Veratrine occurs in the seeds of *Veratrum sabadilla*, and is an amorphous white or greyish-white powder; m.p. 205°. The inhaling of even a minute trace causes irritation of the nostrils. The name veratrine is also given to the mixture of alkaloids (m.p. 150°) obtained from *sabadilla*. It is soluble

in chloroform or alcohol, slightly soluble in ether or amyl alcohol.

1. When placed in an evaporating basin and moistened with concentrated **sulphuric acid,** a deep yellow coloration is obtained, which becomes an intense red on heating.

*2. When a small quantity of veratrine is ground up with about four times its bulk of **sucrose,** and moistened with concentrated sulphuric acid, a yellow coloration is produced, which slowly changes to brown-green, then to a deep green, and finally to a beautiful indigo.

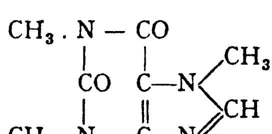
*3. On dissolving in a little concentrated **hydrochloric acid,** a colourless solution is obtained, which on boiling becomes intensely red.

*4. **Froehde's reagent** produces a cherry-red coloration, which gradually turns green. In very small quantities the change of colour is rather slow.

5. **Mandelin's reagent** gives a yellowish-brown coloration, becoming crimson.

6. **Erdmann's reagent** produces a bright yellow colour, which becomes intensely red.

Caffeine or Theine (Trimethylxanthine).



Caffeine or theine is found in coffee and tea and belongs to the purine family. It is generally obtained from tea-dust, and forms beautiful, silky, needle-shaped crystals; m.p. 232-234°. It is soluble in water, alcohol, ether, or chloroform. Caffeine is only a feeble base, its salts being decomposed by excess of water (hydrolysed).

1. Heated in a dry tube caffeine melts, and then sublimes, but when carefully heated, it sublimes much below its melting-point.

***2.** When caffeine is heated to about 180° with **soda lime**, ammonia is evolved, and an alkaline carbonate and cyanide are produced. The cyanide may be distinguished by dissolving in water and applying the usual tests. (See p. 151.)

3. Concentrated **sulphuric acid** produces no change, but on adding a small quantity of powdered **potassium dichromate**, a green coloration gradually appears.

***4. Murexide reaction.**—When caffeine is placed in an evaporating dish and thoroughly moistened with **bromine water** (a large excess should not be added), and the solution evaporated to dryness on the water bath, a yellow residue is left, which becomes crimson on further heating, and is turned a brilliant purple on addition of **ammonia.**

This reaction may also be shown by adding a few drops of concentrated **hydrochloric acid** to some caffeine, and then a crystal of **potassium chlorate** about the size of a pin's head, and evaporating to dryness as above; on adding **ammonia**, the purple coloration is produced. (*Cf.* Uric Acid, § 6, p. 269.)

***5.** Caffeine gives no precipitation with **Mayer's reagent**, and this distinguishes it from most other alkaloids.

6. When fused with **potassium hydroxide** an odour of **trimethylamine** is produced.

Atropine (*l*-Hyoscyamine).

$C_{17}H_{23}NO_3$

This alkaloid is obtained from the leaves and roots of *Atropa belladonna* (Deadly Nightshade). It is isomeric with hyoscyamine. Atropine forms colourless acicular crystals; m.p. 115°. It is slightly soluble in water, readily in alcohol, ether, or chloroform. When applied to the eye it dilates the pupil.†

1. On careful heating, atropine sublimes with very little decomposition.

† Students are advised *not* to try physiological experiments with the alkaloids.

2. Moisten a trace of the base or of its salts with fuming **nitric acid,** and evaporate to dryness on the water bath. Now moisten the residue with a drop of an alcoholic solution of potassium hydroxide. A brilliant violet coloration is produced.

3. Dissolve a little atropine in about half a cubic centimetre of concentrated sulphuric acid, add a small crystal of **sodium nitrite,** and stir with a glass rod. Now add excess of an alcoholic solution of potassium hydroxide, when a beautiful lilac-pink coloration is formed.

4. When warmed with concentrated sulphuric acid, a characteristic odour of the bloom of *spiræa* is produced.

5. Mandelin's, Erdmann's, and Froehde's reagents give no colorations.

6. A yellow precipitate is produced on addition of **mercuric chloride** to an alcoholic solution of atropine.

Berberine.

$C_{20}H_{17}O_4N$

Berberine is obtained as optically-inactive, deep yellow crystals (m.p. 145°), from the roots of *Berberis vulgaris*, or of golden seal. They crystallise with 6 molecules of water and are soluble in water or alcohol, and slightly soluble in ether.

1. Concentrated **sulphuric acid** produces an olive-green colour.

2. **Nitric acid** produces a red-brown shade.

3. **Erdmann's reagent** gives a green colour similar to that obtained with sulphuric acid.

4. **Froehde's reagent** gives a colour intermediate between those of §§ 1 and 2.

Aconitine (Acetyl benzoyl aconine).

$C_{34}H_{47}O_{11}N$

Aconitine is extremely poisonous and is obtained from the root of *Aconitum napellus* (monkshood). It crystallises in

dextro-rotatory rhombic prisms (m.p. 204°), and is slightly soluble in water or benzene, and readily soluble in ether or alcohol.

1. **Acids.**—It produces no colour when dissolved in sulphuric or nitric acid or when evaporated with phosphoric acid.

2. **Erdmann's reagent** gives a pale yellow colour.

3. **Froehde's reagent** gives a yellow colour.

Piperine.

$C_{17}H_{19}O_3N$

This alkaloid occurs abundantly in *Piper nigrum* (black pepper), and is obtained as colourless, monoclinic, optically-inactive crystals (m.p. 129°), which are insoluble in water, and soluble in ether, chloroform or alcohol.

1. Solutions of piperine in concentrated **sulphuric acid** are blood red in colour, but become colourless on dilution.

2. Addition of **formaldehyde** with the sulphuric acid produces a green colour.

3. **Crystal Tests.**—(*a*) Piperine is precipitated from a solution in a drop of acetone by addition of a drop of water, in fine long needles. (*b*) Well-defined prisms of piperine acetate are produced by crystallisation of a solution of a little of the solid alkaloid in warm 30 per cent. acetic acid. Addition of a crystal of sodium acetate assists this.

LIQUID ALKALOIDS.

Nicotine.

$C_5H_7N . C_5H_7N$

Nicotine occurs in tobacco, combined with malic and citric acids, the quantity varying from 0·6 to 8 per cent. When pure it is a colourless fluid, but it rapidly turns yellow and brown

on exposure to air. It boils at 250° with partial decomposition, but is readily volatile with steam, and even with alcohol vapour. Nicotine dissolves readily in water, to which it imparts its penetrating and unpleasant odour, resembling that of a foul tobacco-pipe. Nicotine forms two series of salts, the **monoacid** salts, which are neutral to litmus, and the **diacid** salts, which have an acid reaction.

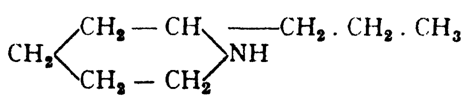
***1.** On gently warming with concentrated **hydrochloric acid** a light brown coloration is produced, which on addition of a drop of concentrated **nitric acid**, turns orange.

***2.** When a trace of nicotine is moistened with one drop of **formaldehyde**, and then with one or two drops of **nitric acid**, a brilliant pink coloration is obtained. (Distinction from coniine.)

3. Of the general reagents Mayer's is the most delicate, giving a precipitate of $C_{10}H_{14}N_2$, HgI_4 from extremely dilute solutions of nicotine.

***4. Mercuric chloride** produces a white precipitate which quickly turns light yellow.

Coniine (d. α-propyl Piperidine).



Coniine is the poisonous principle of hemlock (*Conium maculatum*). It is an oily liquid (b.p. 170°), possessing a very unpleasant odour, like that of a foul tobacco-pipe; it also has a peculiar "mousy" smell, which is especially marked when coniine is dissolved in water. Coniine is readily volatile with steam, and is easily soluble in water and practically all organic solvents. It is a very strong base, and forms neutral salts with acids. The chief interest of coniine lies in the fact that it was the first optically-active plant alkaloid to be synthesised.

***1.** Concentrated **sulphuric acid** and **potassium dichromate** quickly produce a grass-green coloration.

***2.** A few drops of alcohol are added to a trace of coniine contained in an evaporating dish, and then two or three drops of **carbon disulphide**; on allowing to stand a minute or two, and then adding a drop of very dilute **copper sulphate,** a brown coloration is produced. (Distinction from nicotine.)

***3.** Dissolve a drop of coniine in about 1 c.c. of alcohol, and add an equal volume of water. On now adding a few drops of **phenolphthalein** a pink coloration is produced. Nicotine only shows this test when the alcoholic solution is *very* largely diluted with water. The test may be applied to a trace of coniine, contained in a watch glass, by adding two or three drops of alcohol, a little water, and about 0·5 c.c. of a solution of phenolphthalein.

4. Mercuric chloride produces a white precipitate, which does not turn yellow, as does the corresponding precipitate produced with nicotine.

5. Froehde's reagent gradually produces a pinkish-yellow coloration.

Detection of the Alkaloids.

Having by means of the "general reactions" (p. 334) found that the substance under examination is an alkaloid, or an alkaloid mixed with other substances, inorganic or organic, it is now necessary to determine which of the many alkaloids it may be. If it is mixed with other substances, it may be necessary, and is always advisable, to separate it first before applying special tests. In order to do this, the mixture is made alkaline with caustic alkali, evaporated to dryness, and extracted several times with small quantities of ether. On evaporating or distilling off the ether, the alkaloid will be obtained free from inorganic and most organic contaminations. **Morphine,** it must be remembered, is not soluble in ether, and must be extracted with hot amyl alcohol. If aniline, pyridine,

or quinoline is present along with non-volatile alkaloids, it will be necessary first to subject the alkaline mixture to steam distillation. Having done this, evaporate the residue to dryness, and extract with ether as already explained.

The tests enumerated in the table which follows (pp. 352, 353) should be applied, in the order given, to small portions of the alkaloids thus obtained, placed on a white porcelain tile, or, better, in an evaporating dish, because then heat may be more readily applied.

One of the best methods for applying tests to the ethereal solution is to place two or three drops in an evaporating basin and allow the ether to evaporate spontaneously, or by gentle warming, then to add the reagent to the residue. A fresh portion must be taken for each test. If the substance under examination is a solution of a salt of an alkaloid, then the alkaloid may be precipitated by addition of sodium carbonate or caustic alkali.† The test can then be applied to separate small portions of the precipitated alkaloid. Or the solution may be rendered alkaline, and evaporated to dryness on a water bath, the residue being extracted with ether as already described.

In many cases the tests in the table will be sufficient to prove which alkaloid is present, but in some cases it will be found necessary to apply confirmatory tests, *e.g.* in the case of quinine and cocaine, which give no very characteristic reactions with the reagents enumerated. Such confirmatory tests may be taken from the reactions found under the head of the particular alkaloid.

At the end of the table the reactions of **salicin, digitalin, acetanilide, phenacetin,** and **antipyrin** have been included, it being of interest to compare the reactions of these substances with those of the alkaloids; also because these substances, with the exception of salicin, are soluble in ether, and might, therefore, be mistaken for alkaloids.

† Owing to the solubility of morphine in caustic alkali, if its presence is suspected ammonium hydroxide should be employed as the precipitant, instead of caustic alkali.

TABLE SHOWING BEHAVIOUR OF THE ALKALOIDS, GLUCOSIDES, ETC., WITH VARIOUS REAGENTS.

Alkaloid.	Conc. H_2SO_4.	Conc. H_2SO_4, then sprinkle with powdered $K_2Cr_2O_7$.	Conc. HNO_3. (sp. gr. 1·40.)	Froehde's reagent.	Erdmann's reagent.	Mandelin's reagent.
Morphine .	Pale rose-red, changing to yellow.	Greenish-brown.	Orange-red, yellow on heating.	Purple, becoming green, and finally brownish-yellow.	Brown.	Brownish-purple, becoming grey.
Apomorphine .	—	Olive-green, becoming brown-green.	Brilliant purple-red, changing to mahogany-brown.	Deep green, turning bluish.	—	Greyish or greenish-blue.
Codeine . .	Colourless; slight blue on warming, one drop HNO_3 causing deep red.	Dirty brown.	Deep yellow.	Dirty green, becoming bright green, then blue, finally yellow.	Yellow to green.	Greenish-grey to greyish-blue.
Narcotine .	Yellow; on warming, intense red, changing to violet.	Brown.	Orange to yellow.	Deep grass-green.	Orange - yellow, turning momentarily pink and again yellow.	Orange, becoming pink.
Cocaine .	—	Dirty brown.	No colour.	No colour.	No colour.	—
Quinine .	Blue fluorescence on diluting.	Immediate grass-green.	Blue fluorescence.	No colour.	Light yellow.	No colour; on adding a drop of nitric acid, violet.
Quinidine .	—	Grass-green.	Blue fluorescence.	—	—	No colour; on adding a drop of nitric acid, violet.
Cinchonine .	—	Grass-green.	No colour.	No colour.	No colour.	No colour; on adding a drop of nitric acid, violet.
Strychnine .	—	Violet to blue.	Yellow on warming.	No colour.	No colour.	Blue, changing to brilliant violet; red on warming.

Brucine .	Pale rose-red, slowly turning yellow.	Red-brown.	Intense blood-red, becoming yellowish.	Light red to deep reddish-brown.	Pink.	Rose-red, quickly changing to orange.
Veratrine .	Yellow; intense red on warming.	Green to greenish-brown.	Pink, quickly becoming yellow.	Cherry-red, changing to green.	Bright yellow, becoming intense red.	Yellowish-brown becoming crimson.
Caffeine .	—	Slowly turns green.	No colour.	No colour.	No colour.	—
Atropine .	—	Grass-green.	Yellow, see § 2, p. .	No colour.	No colour.	—
Nicotine .	Brown on warming.	Slowly brownish-green.	No colour.	No colour.	No colour.	—
Coniine .	—	Grass-green.	No colour.	Gradually pinkish-yellow.	No colour.	—
Aconitine .	Pale yellow.	—	No colour.	Pale yellow	Pale yellow.	—
Berberine .	Olive-green.	—	Red-brown	Brown-green	Olive-green.	—
Piperine .	Deep red. Colourless on dilution.	—	—	—	—	—
			NON-ALKALOIDS.			
Salicin .	Blood-red coloration.	Reddish-brown, becoming mahogany.	Yellow.	Violet.	Bright red, edges becoming purple.	Purple red.
Digitalin .	Golden-yellow, then brown to red.	Brown, slowly turning green.	Deep yellow.	Brown, becoming cherry-red.	Brown.	Mahogany-brown becoming deep cherry-red.
Acetanilide .	—	Bright red, quickly becoming grey, red reappearing when rubbed with glass rod.	Yellow on warming.	—	—	Orange, becoming red, finally grey.
Phenacetin .	—	Gradually becomes grass-green.	Deep yellow.	—	—	Very pale blue.
Antipyrin .	—	Gradually becomes grass-green.	No colour in cold; on heating, deep carmine.	—	—	Light blue, slowly fading.

Students should not make use of the table until they have carefully worked through the individual reactions, because the reactions, although highly characteristic, are difficult to describe accurately. The changes of shade being often very gradual, the novice is therefore very apt to misinterpret what he observes.

SUMMARY.

The student, who has carefully worked through the organic reactions set out in this book, will have found that the methods of separation employed in organic chemistry are entirely different from those employed in inorganic chemistry. In organic chemistry the number of compounds is vast and the properties of the substances depend to a very marked extent on the nature and positions of the various groups. For example, phenol, although not a strong enough acid to decompose sodium carbonate, has yet sufficiently strongly marked acid properties to cause it to react with sodium hydroxide to form a soluble sodium salt. Addition of a negative group, such as — NO_2, increases its acidic properties to such an extent that the nitrophenols dissolve in sodium carbonate with formation of a sodium salt. It is obvious, then, that methods of separation which might have been employed in separating phenol, say, from acetic acid, will require to be modified in order to separate nitrophenol from acetic acid.

Again, aniline has basic properties, but the basicity becomes less and less marked as halogen or other negative groups replace the hydrogen atoms of the benzene nucleus, until finally the basic character is entirely lost.

As a rule in dealing with an unknown organic substance, the first thing to do is to ascertain what elements are present, then to test its solubility in sodium carbonate, caustic alkalis, or acids. By this procedure the substance can generally be referred to some definite group, *e.g.* acids, phenols, amines, etc. Certain dry reactions such as heating in a dry tube and ignition with soda lime, should also be tried, and the action of concentrated sulphuric acid is also often helpful.

Speaking generally, amino compounds may be separated from phenols by rendering the mixture alkaline with sodium hydroxide, and either distilling the base thus set free in a current of steam, or else extracting it with ether. Or the mixture may be acidified with hydrochloric acid, when a non-volatile salt of the amino compound is produced, and the phenol remaining in the free state may be separated by extraction with ether or steam distillation.

Again, phenol may be separated from acids by adding a slight excess of sodium carbonate, when the acids will form sodium salts, whereas phenol does not. In separating acids from one another it is often necessary to use the different behaviour of their metallic salts, *e.g.* calcium tartrate is precipitated from cold water (p. 256), whereas calcium citrate (p. 257) only comes down from boiling solutions or after the addition of alcohol. Or the acids may be converted into their esters, which may then be separated by fractional distillation. It will be thus seen that it is quite impossible to give a general scheme for separation of organic substances. *Separations can only be carried out by the student having an intimate acquaintance with theoretical as well as with practical chemistry.*

To learn by rote the reactions of the compounds set out in this book would only be a feat of mental gymnastics, and would do the student absolutely no good. But to learn and digest the reactions which are common to acids or bases or phenols, etc., and to understand the modifying effect of the addition or substitution of different radicals, is not only useful but essential.

The author trusts that the students who use this book will not consider that, because they have worked through the organic reactions contained in it, they *know organic chemistry.* The student is recommended also to work through a systematic practical course of "Organic Preparations," and at the same time to study the theory.

APPENDIX.

APPENDIX.

SOLUBILITIES.

THE terms **soluble** and **insoluble** are more or less relative, no substance being *absolutely* insoluble. For example, **barium sulphate** is looked upon as one of the most insoluble of salts, 1 part dissolving in 800,000 parts of water. Compared with this, **strontium sulphate**, which is also said to be insoluble in water (1 : 7000), is a fairly soluble substance; while **calcium sulphate** (1 : 430) may be said to be soluble in water. On the other hand, calcium sulphate is almost insoluble when compared with **potassium iodide**, which is soluble in less than its own weight of water.

The solubility of a substance in acids is not generally a case of simple solution. Solution in acids is more often produced by an exchange of ions and formation of a non-ionised (or very slightly ionised) acid; *e.g.* when **aluminium phosphate** is suspended in water, it dissolves slightly, and becomes ionised into the ions $Al^{\cdots}$ and PO_4'''. On addition of **hydrochloric acid**, which in solution is highly ionised, the $H^{\cdot}$ **cations** of the acid unite with the **anion** of aluminium phosphate to form **phosphoric acid**, which is very feebly ionised. The equilibrium existing between the aluminium ions and the phosphate ions is thus disturbed, so that more of the aluminium phosphate goes into solution to be in turn ionised, so long as there is an excess of free $H^{\cdot}$ cations (*i.e.* an excess of hydrochloric acid), to form phosphoric acid. The Cl' and $Al^{\cdots}$ ions remain chiefly in the ionised condition, but can on concentration be obtained as **aluminium chloride.**

Again, when hydrochloric acid acts upon **cadmium sulphide** the cadmium sulphide goes into solution, and very feebly ionised **hydrogen sulphide** is produced. A small portion of the hydrogen sulphide, owing to its solubility, will remain in solution, partly in the non-ionised and partly in the ionised condition. Owing, however, to its volatility, the main portion passes out into the air, and on raising the temperature, the whole of it will be evolved (*cf.* p. 20).

The solubility of salts in acids is limited; only the difficultly

soluble **salts** of slightly ionised acids (*i.e.* weak acids) will dissolve in strong acids; salts of highly ionised acids (*i.e.* strong acids) are not dissolved by other highly ionised acids: *e.g.* **silver** and **mercurous chloride** are not soluble in **nitric acid.** Neither **barium** nor **strontium sulphate** is soluble in **hydrochloric acid,** although, if the acid is in very large excess **mass action** comes into play (see p. 22).

REAGENTS.

Distilled water must always be employed for preparing the solutions of reagents required in analysis.

The reagents should always be of the standards of purity specified for analytical work. The letters A.R. indicate an "Analytical Reagent" conforming to these standards.

As has already been stated on p. 34, it is best to prepare all the reagents of equivalent or known strength, because if the strengths of the various solutions are known, it is much

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NOTES TO PAGE 361.

[1] Potassium platinichloride is insoluble in water or dilute acids. Potassium cobaltinitrite is also insoluble in water, but is decomposed by acids.

[2] Ammonium platinichloride is insoluble in water or dilute acids. Ammonium magnesium-phosphate and ammonium magnesium-arsenate are insoluble in water, but are decomposed by acids.

[3] Anhydrous chromic chloride, bromide, and oxide are insoluble both in water and in acids.

[4] The sulphides of nickel and cobalt are slightly soluble in hydrochloric acid, but dissolve readily in *aqua regia.*

[5] Silver sulphide is only soluble in nitric acid.

[6] Mercurous nitrate will only form a clear solution in water containing nitric acid (*cf.* note 9).

[7] Mercuric sulphate and nitrate only form clear solutions when an excess of free acid is present. Mercuric sulphide only dissolves in *aqua regia.*

[8] All cuprous salts are insoluble in water.

[9] Owing to the weak basicity of bismuth its salts are hydrolysed in aqueous solution with formation of insoluble oxy-salts. In order to obtain a clear solution it is therefore necessary to have an excess of acid present. The same remarks apply to antimony and mercury.

[10] Gold and platinum sulphides are only soluble in *aqua regia.*

[11] Lead chloride, bromide, and iodide only dissolve in hot water, from which they recrystallise on cooling.

[12] Basic aluminium acetate is insoluble in water, but soluble in acids; the same is the case with ferric acetate.

TABLE OF SOLUBILITIES. (For Notes, see p. 360.)

W = soluble in water. A = insoluble in water, but soluble in acids. WA = difficultly soluble in water, but readily soluble in acids. aw = difficultly soluble in both water and acids. I = insoluble in water and in acids.

Anion. / Cation	F'.	Cl'.	Br'.	I'.	CN'.	NO_3'.	ClO_3'.	$CH_3.CO_2'$.	S''.	CO_3''.	SiO_3''.	SO_4''.	CrO_4''.	$\{BO_3'''$. $\{BO_2'$.	PO_4'''.	AsO_4'''.	AsO_3'''.	$Fe(CN)_6'''$.	$Fe(CN)_6''''$.
[1] K˙	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Na˙	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W
[2] NH˙₄	W	W	W	W	W	W	W	W	W	W	—	W	W	W	W	W	W	W	W
Ba˙˙	aw	W	W	W	WA	W	W	W	W	A	A	I	A	A	A	A	A	—	WA
Sr˙˙	aw	W	W	W	W	W	W	W	W	A	A	I	WA	A	A	A	A	—	W
Ca˙˙	aw	W	W	W	W	W	W	W	W	A	A	aw	WA	A	A	A	A	W	W
Mg˙˙	aw	W	W	W	W	W	W	WA	W	A	A	W	W	WA	A	A	A	W	W
Al˙˙˙	W	W	W	W	—	W	W	W[12]	—	—	aw	W	—	A	A	A	—	—	—
[3] Cr˙˙˙	W	W	W	W	A	W	W	WA	—	—	A	W	A	A	A	A	—	—	—
Fe˙˙˙	W	W	W	—	—	W	W	A[12]	—	—	A	W	W	A	A	A	A	W	I
Fe˙˙	WA	W	W	W	aw	W	W	W	A	A	A	W	—	A	A	A	A	I	I
Mn˙˙	A	W	W	W	A	W	W	WA	A	A	A	W	W	A	A	A	A	I	A
Zn˙˙	WA	W	W	W	A	W	W	W	A	A	A	W	W	A	A	A	—	A	aw
Ni˙˙	WA	W	W	W	aw	W	W	W	A[4]	A	A	W	A	A	A	A	A	I	I
Co˙˙	WA	W	W	W	aw	W	W	W	A[4]	A	A	W	A	A	A	A	A	I	I
Ag˙	W	I	I	I	I	W	W	A	A[5]	A	A	WA	A	A	A	A	A	A	I
Hg˙	—	I	I	I	—	W[6]	W	A	—	A	—	WA	A	—	A	A	A	—	—
[7] Hg˙˙	WA	W	W	A	W	W	W	A	A	A	—	W	WA	—	A	A	A	—	—
[8] Cu˙˙	A	W	W	I	I	W	W	W	A	A	—	W	W	A	A	A	A	—	I
Cd˙˙	WA	W	W	W	A	W	W	W	A	A	A	W	W	WA	A	—	—	—	—
Pb˙˙	A	W[11]	W[11]	W[11]	A	W	W	W	A	A	A	I	I	A	A	A	—	WA	A
[9] Bi˙˙˙	W	A	A	A	—	A	W	A	A	A	A	A	A	A	A	A	—	—	—
Sn˙˙	W	W	—	W	—	W	W	A	A	—	—	W	A	A	A	—	—	I	I
Sn˙˙˙˙	W	W	—	W	—	—	—	—	A	—	—	—	—	—	A	A	A	—	I
Sb˙˙˙	W	A	A	WA	—	—	—	A	A	—	—	A	A	—	A	A	—	—	—
Au˙˙˙	—	W	W	A	W	—	—	—	A[10]	—	—	—	—	—	—	—	—	—	—
Pt˙˙˙˙	—	W	W	I	W	W	—	—	A[10]	—	—	W	—	—	—	—	—	—	—

easier to gauge how much of a solution may be required to neutralise a given solution. Thus, supposing 5 c.c. of sulphuric acid of 4N strength has been added to the solution and it is afterwards required to neutralise it. If the alkaline solution is of an equivalent strength, then 5 c.c. would be required to render the mixture neutral. It is not necessary to make the solutions up absolutely equivalent as in quantitative analytical work ; so long as they are approximately equivalent, that is sufficient. For making solutions of solids—provided the materials are fairly pure, there is no great difficulty in preparing the solutions. With liquids, such as hydrochloric acid and ammonia, it is a little more difficult, but, by using the curves, Figs. 28 and 29, it will be found possible to prepare solutions which are very nearly equivalent in strength. For most purposes solutions of 4N strength will be found to answer, and, where not otherwise stated, this strength is understood as being used in this book.

In the curves the vertical distances show the density of the solution of acid or of ammonia, and the horizontal distances the number of cubic centimetres which it is required to make up to 1 litre with water in order to prepare a normal solution.

Thus suppose, *e.g.*, that the density of the sulphuric acid has been found by means of an hydrometer to be 1·52. (This is approximately the density of a solution obtained by adding 1 volume of concentrated sulphuric acid to 1 volume of water.) Trace an imaginary horizontal line (Fig. 28) from the density on the vertical line ; it will be found to cut the sulphuric acid curve at a certain point : now from this point trace an imaginary line perpendicularly downwards, and it will be found to cut the horizontal line between 50 and 55. The exact position of the line is 52·5—that is to say, in order to prepare a normal solution of sulphuric acid 52·5 c.c. of this acid must be run into a litre flask, and the flask filled up to the 1 litre mark with distilled water. In order to obtain 4N sulphuric acid, four times this quantity of acid would require to be used. The quantity of the other acids which it is required to use can be found in a similar manner.

Acids.

Sulphuric Acid (**Concentrated**).—It is advisable always to use the pure A.R. acid.

Sulphuric Acid (**Dilute**).—A normal solution contains 49 grms. of pure acid to the litre, and a 4N solution 196 grms. Pour the quantity of the given acid containing this amount of pure acid (obtained from the curve, Fig. 28) into about half a litre of water, and after cooling make up to the litre mark with distilled water. Suppose the density of the sulphuric acid is

1·2, then from Fig. 28 it will be seen that 151 c.c. of this acid diluted to 1 litre will make a litre of normal acid. Therefore to obtain a 4N solution 604 c.c. would require to be diluted to 1 litre.

Hydrochloric Acid (Dilute).—Prepare a 4N solution. A normal solution contains 36·45 grms. of gaseous HCl per litre, a 4N 145·8 grms. Take the density of the acid, and from this find out how many cubic centimetres must be diluted to 1 litre in order to make a 4N solution (Fig. 29).

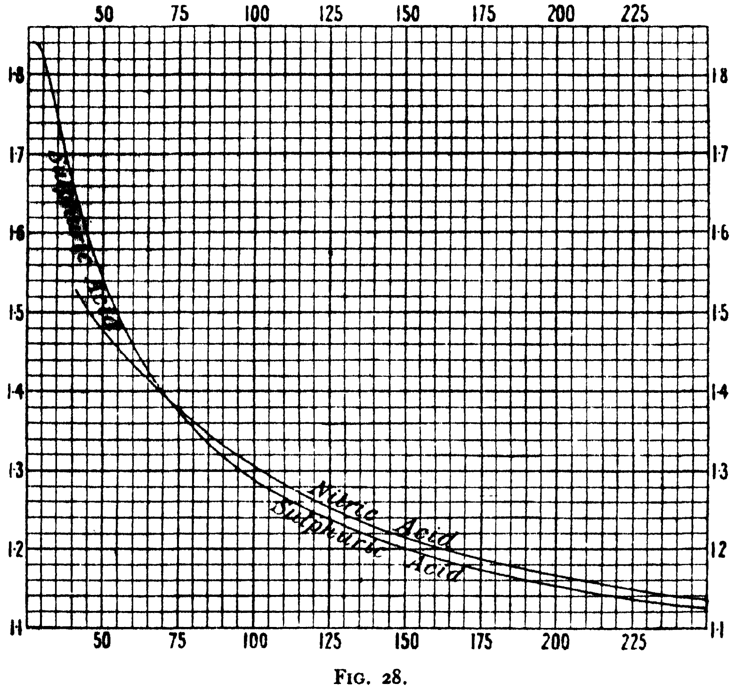


FIG. 28.

Nitric Acid (Dilute).—Prepare a 4N solution. A normal solution contains 63 grms. of pure acid per litre, a 4N contains 252 grms.

Acetic Acid (Dilute).—Prepare a 4N solution. A normal solution contains 60 grms. of pure acid per litre, a 4N solution 240 grms. The curve for acetic acid (Fig. 29) shows that for specific gravities above 1·055 two different quantities may be read for the same specific gravity. To avoid this ambiguity it will therefore be necessary first to dilute the acid with water till the specific gravity falls just below 1·055.

Oxalic Acid (Solution).—Prepare a 2N solution of the acid containing 126 grms. of oxalic acid crystals per litre.

Sulphurous Acid.—Prepared by saturating distilled water with the gas. Liquid sulphur dioxide can be obtained in siphons, from which the gas may be obtained as required. The saturated solution is about 3·7N.

Hydrofluoric Acid.—This is best used as purchased; the solution usually contains about 30 per cent. of HF, about 1·5N.

Hydrofluosilicic Acid is tiresome to prepare, and so is best purchased.

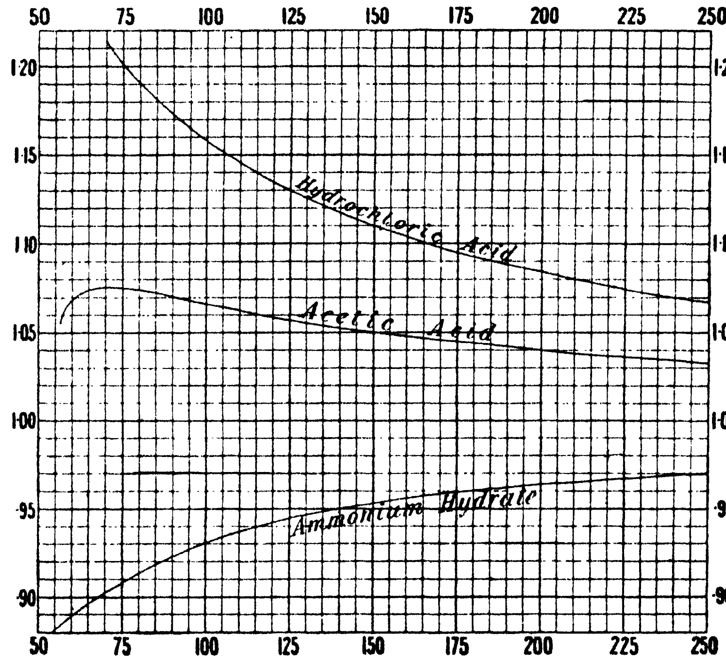


FIG. 29.

Aqua Regia must always be prepared as required by mixing 1 volume concentrated nitric acid with 4 volumes concentrated hydrochloric acid.

Chlorine Water.—Pass chlorine gas into distilled water until no more is absorbed. The bottle in which the chlorine water is kept should be painted black. A saturated solution is about 0·2N.

Bromine Water.—Add bromine to distilled water, and shake up till a portion remains undissolved. Keep in a cool place,

in a well-stoppered bottle containing a little undissolved bromine. The solution is about 0·5N.

Hydrogen Sulphide.—Either the gas may be obtained from a Kipp's apparatus or a saturated solution of the gas in water may be used. Fig. 30 shows an apparatus from which either the gas or a saturated aqueous solution can be obtained. The apparatus consists of a bottle A containing ferrous sulphide, which has a tubulus on either side, near the bottom, by means of which it is connected with the reservoir B (represented in the sketch by the dotted lines) and the flask C. D is a wash bottle containing a little water, the outlet tube of which is connected with a tube *d*

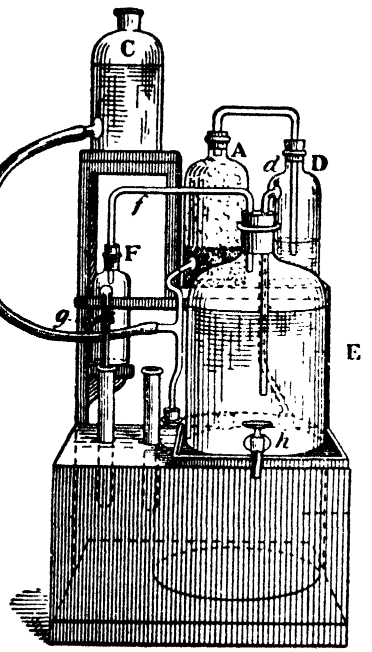


FIG. 30.

passing nearly to the bottom of the bottle E (about 3 or 4 litres capacity) filled with distilled water. A second tube *f*, which does not dip below the surface of the water, passes into a small "catch" bottle F. This bottle has an outlet tube to which is attached, by means of a piece of rubber, a glass tube about 8 inches long; *g* is a small brass clip which serves to close the rubber tube.

Should an aqueous solution of hydrogen sulphide be required,

it can be obtained by turning on the tap *h*, whereas one can get a supply of the gas by opening the clip *g*. When the apparatus is freshly charged, the clip *g* should be opened and a rapid current of the gas bubbled through the water in E for a few minutes. By this means the air on the surface of the water is driven out, and on closing the clip the gas will be absorbed until the water is saturated. As soon as the water is completely saturated, the pressure of the gas drives the acid up into C, and all action ceases. As there is no air present in E, no oxidation can take place, and the solution, even if the apparatus is standing in strong light, deposits only a trace of sulphur.

All the rubber connections of the apparatus should be carefully wired on, so that no leakage can take place, and it will usually be found best to keep the apparatus with the bottle C always in the position represented in the sketch. By so doing, the aqueous solution of hydrogen sulphide is always saturated.

In order to prevent the solution in E from being driven back into the wash bottle D, should a back pressure be set up (*e.g.* owing to rise of atmospheric temperature, and consequent decrease of solubility of the gas in water), a layer of mercury is placed in D below which the tube *d* just dips. The mercury acts as a seal, and prevents the solution from being driven back.

For convenience the stand contains two holes in which test-tubes may be placed while passing the gas.

Hydrochloric acid (1 part acid and 2 parts water) should be used to generate the gas, because when sulphuric acid is employed there is a tendency for ferrous sulphate to crystallise out and to clog the apparatus.

Bases, etc.

Potassium or Sodium Hydroxide.—4N solution. Normal solution of NaOH contains 40 grms. to the litre and 4N 160 grms. per litre.

Normal solution KOH contains 56 grms. per litre, 4N contains 224 grms. per litre.

Ammonium Hydroxide.—4N solution. This solution can be made up by taking the density and then using the curve on Fig. 29. Normal solution contains 17 grms. ammonia gas or 35 grms. NH_4OH.

Calcium Hydroxide (Lime Water).—Mix an excess of slaked lime with water, and allow to settle; then siphon off the clear solution, which must be kept in a well-stoppered bottle. The saturated solution is about $\frac{N}{32}$.

Barium Hydroxide.—The crystallised salt contains water of crystallisation $Ba(OH)_2 8H_2O$, but it is also usually very much

contaminated with carbonate. The best way is to prepare a cold saturated solution by shaking up with cold water until no more is dissolved, and then filtering from the insoluble barium carbonate. This solution contains about 50 grms. to the litre, it is therefore about 0·3N.

Ammonium Sulphide.—Saturate 1 volume of ammonium hydroxide with hydrogen sulphide; when saturated, mix with 2 volumes of ammonium hydroxide of the same strength, and dilute with about 5 volumes of water.

Yellow Ammonium Sulphide.—Add to every litre of the colourless ammonium sulphide 10 grms. of flowers of sulphur.

Salts, etc.

Ammonium Chloride.—4N solution; dissolve 214 grms. in 1 litre of water.

Ammonium Oxalate.—N solution; dissolve 73 grms. of crystallised salt $(COONH_4)_2$, $2H_2O$ in 1 litre of water.

Ammonium Sulphate.—2N solution; 132 grms. crystallised salt to 1 litre.

Ammonium Acetate.—2N solution; 154 grms. crystallised salt to 1 litre.

Ammonium Carbonate.—80 grms. solid ammonium carbonate and 32 c.c. ammonium hydroxide (sp. gr. 0·88) to 1 litre of water.

Ammonium Nitro-Molybdate. — Dissolve 150 grms. ammonium molybdate in 1 litre of water, and then pour into 1 litre of nitric acid (sp. gr. 1·2); now dissolve 100 grms. of ammonium nitrate in this mixture, ~~warm for 1 hour at about 60°~~, allow to stand over night, and decant from any residue.

Potassium Chromate.—2N solution; 194 grms. per litre.

Potassium Dichromate.—0·5N solution; 73·59 grms. per litre.

Potassium Cyanide.—N solution; 65 grms. per litre. This solution does not keep very well, so should only be prepared in small quantities at a time.

Potassium Ferrocyanide.— $K_4Fe(CN)_6$, $3H_2O$. N solution; 105·5 grms. per litre.

Potassium Ferricyanide.—N solution; 109·5 grms. per litre. Solution should be prepared in small quantities as required.

Potassium Nitrite.—Solution should be prepared as required. A normal solution contains 85 grms. per litre.

Potassium Thiocyanate.—N solution; 97 grms. per litre.

Potassium Iodide.—Should only be prepared in small quantities at a time. A normal solution contains 166 grms. to the litre.

Potassium Pyroantimonate.—Boil 50 grms. potassium antimonate with concentrated nitric acid until no more red fumes are evolved. Allow to settle, and decant off the liquid, and wash the antimonic acid several times with water by decantation. Then boil the residue for 5 or 10 minutes with strong potassium hydroxide (1 part H_2O and 1 part KOH). Cool the mixture, and filter off the excess of potassium hydroxide on an asbestos filter. The acid potassium salt $KHSbO_4$, $6H_2O$ may now be dissolved in 500 c.c. warm water, and can then be used as a reagent for sodium.

Potassium Carbonate.—4N solution ; 276 grms. of K_2CO_3 per litre ; the anhydrous salt to be used.

Sodium Carbonate.—N solution , dissolve 53 grms. anhydrous sodium carbonate per litre.

Sodium Cobaltinitrite may be prepared by dissolving 150 grms. sodium nitrite in 150 c.c. of water with heating. The solution is then cooled to about 50° C., and 50 grms. of crystallised cobalt nitrate added ; as soon as the cobalt nitrate has dissolved, 50 c.c. of 50 per cent. acetic acid are added. After shaking up, the brown solution is filtered to separate any *potassium* cobaltinitrite which may have been formed from impurities present, and a current of air is aspirated through it to remove oxides of nitrogen. 150 c.c. of alcohol are now added, the mixture being allowed to stand for about half an hour with occasional shaking, and then filtered. The sodium cobaltinitrite, which is thus obtained as a more or less crystalline powder, is washed with alcohol and dried. In employing it as a test for potassium or ammonium about 0·25 grm. is dissolved in about 2 c.c. of water. It decomposes when kept in solution.

Sodium Phosphate.—Na_2HPO_4, $12H_2O$. 0·5N solution ; 59·6 grms. per litre.

Sodium Thiosulphate.—$Na_2S_2O_3$, $5H_2O$. 0·5N solution ; 62 grms. per litre. As this solution gradually decomposes, it is better to prepare it as required.

Sodium Nitroprusside.—This solution should be prepared as required by dissolving a few crystals in a little water.

Barium Chloride.—$BaCl_2$, $2H_2O$. N solution ; 122 grms. per litre.

Bleaching Powder Solution.—Shake up bleaching powder with water, allow to stand, and decant or filter off the clear fluid.

Borax Solution (to test for Glycerol).—Dissolve 5 grms. of crystallised **borax** in 1 litre of water. Now add sufficient of an alcoholic solution of **phenolphthalein** to produce a rose-red coloration.

Calcium Chloride.—$CaCl_2$, $6H_2O$. 2N solution; 219 grms. per litre.

Calcium Sulphate.—Prepare a saturated solution by shaking up with water; allow to stand until the excess of calcium sulphate has settled, and siphon off the clear solution.

Cobalt Nitrate.—0·5N; 72·5 grms. of the crystalline salt per litre.

Copper Sulphate.—N; 125 grms. of the crystalline salt per litre.

Ferrous Sulphate.—Prepare a solution as required by shaking up the crystallised salt with cold water. It is better to use ferrous ammonium sulphate, because it is less easily oxidised.

Ferric Chloride.—N; 54 grms. of ferric chloride and 5 c.c. of concentrated hydrochloric acid per litre. Solutions of ferric chloride are normally acidic owing to the formation of hydrochloric acid by hydrolysis. It is desirable therefore that when ferric chloride is used as a reagent for substances such as benzoic or salicylic acid, it should be neutralised. To a 2 per cent. solution of ferric chloride are therefore added a few drops of a dilute solution of ammonia. The mixture is then boiled to remove the excess of ammonia, any precipitated ferric hydroxide being converted into the colloidal state. The solution may be filtered if necessary, cooled, and then used.

Fusion Mixture.—Grind together in a mortar equal weights of sodium and potassium carbonates.

Lead Acetate.—$(CH_3 . COO)_2Pb$, $3H_2O$. N solution; 190 grms. per litre.

Gold Chloride.—0·1N; 10·2 grms. per litre.

Magnesium Chloride.—2N; 203 grms. per litre.

Magnesium Sulphate.—$MgSO_4$, $7H_2O$. 2N; 246 grms. per litre.

Magnesia Mixture.—Dissolve separately 100 grms. of magnesium chloride ($MgCl_2$, $6H_2O$) and 250 grms. of ammonium chloride in 1 litre of water, and add 300 grms. of ammonia (sp. gr. 0·880). Filter or decant off the clear liquid after two days.

Mercuric Chloride.—0·5N; 68 grms. per litre.

Mercurous Nitrate.—N. Dissolve 200 grms. mercury in just sufficient moderately strong nitric acid, and dilute to 1 litre with

water. Place a little metallic mercury in the bottle containing the solution.

Silver Nitrate.—0·1N; 17 grms. per litre.

Stannous Chloride.—$SnCl_2$, $2H_2O$. 2N. Dissolve 225 grms. stannous chloride in 500 c.c. 4N hydrochloric acid, and dilute to 1 litre. Place some fragments of metallic tin in the bottle containing the solution. Or dissolve 118 grms. tin in concentrated hydrochloric acid, having a piece of platinum foil in contact with the tin, and make up to 1 litre, adding concentrated hydrochloric acid if the solution becomes opalescent. Preserve in a well-stoppered bottle in contact with granulated tin. The strength of this reagent does not remain constant.

Stannic Chloride.—2N. Take the strong stannous chloride solution prepared as above, containing 118 grms. of tin, and add bromine water to it until it is just brown. Now heat on sand bath in draught cupboard until it becomes colourless. Make up to 1 litre.

Hydrogen Platinichloride.—0·1N; with respect to platinum; 10·66 grms. per litre.

Other Reagents.

Fehling's Solution.—(*a*) 69·28 grms. of copper sulphate crystals are dissolved in 1 litre of water.

(*b*) 350 grms. of Rochelle salt and 100 grms. of sodium hydroxide are dissolved in 1 litre of water.

Equal volumes of solutions (*a*) and (*b*) are mixed and used as required. Each 500 c.c. is equivalent to about 0·25 grm. of dextrose.

Indigo Solution.—Gently warm a mixture of 4 grms. indigo and 50 c.c. conc. sulphuric acid, then allow to stand for 24 hours, and make up to 1 litre with distilled water, and filter.

Nessler's Reagent is prepared by first dissolving 35 grms. of potassium iodide and 12·5 grms. of mercuric chloride in 850 c.c. of water, 120 grms. of sodium hydroxide being then dissolved in the resulting solution. The liquid is cooled, and a saturated solution of mercuric chloride is added drop by drop, with continual stirring, until a small quantity of the red precipitate remains. Dilute to 1 litre, and allow to settle. Finally, decant clear liquid into a bottle, and keep in a dark place.

Oxalic Acid (Test for Urea).—Prepare a cold saturated solution.

Starch Paste.—Shake up 0·5 grm. of soluble starch into a thin paste with cold water. Pour into 100 c.c. of boiling water,

and continue to boil for a few minutes. Allow the liquid to stand till cold, and filter. Starch paste may be kept for some weeks if about 1 c.c. of chloroform be added to it. The iodine reaction is, however, more sensitive when it is freshly prepared.

Schiff's Reagent.—Make a dilute solution of fuchsine, and pass sulphurous acid into it till the colour is destroyed; preserve in a well-stoppered bottle.

Litmus Solution.—Digest 100 grms. of litmus with 500 c.c. hot water. Allow to stand over night, and filter. Now add 300 c.c. of methylated spirit to the solution, filter on the next day and dilute with water to 1 litre.

Phenolphthalein.—Dissolve 5 grms. phenolphthalein in 100 c.c. of warm methylated spirit, and dilute to 1 litre with a mixture of equal volumes of methylated spirit and water.

Methyl Orange.—Dissolve 2 grms. methyl orange in 200 c.c. methylated spirit, and dilute to 1 litre with water.

Brucine (Test for Nitric Acid).—Dissolve 0·5 grm. brucine in 200 c.c. concentrated sulphuric acid. This solution does not keep very well.

Denigè's Citric Acid Test.—Add 5 grms. yellow mercuric oxide to 20 c.c. concentrated H_2SO_4 and 100 c.c. water.

Mercury Thiocyanate Reagent.—Dissolve 30 grms. of mercuric chloride and 33 grms. of ammonium thiocyanate in 50 c.c. of water at room temperature.

Triple Nitrite Reagent.—Dissolve 20 grms. of sodium nitrite, 9·1 grms. of copper acetate, 16·2 grms. of lead acetate and 2 c.c. of acetic acid in 50 c.c. of water, and store in a well-stoppered bottle.

Uranyl-Zinc Acetate Reagent (for Sodium).—Dissolve with the aid of heat (*a*) 10 grms. of uranyl acetate in 6 grms. of 30 per cent. acetic acid, diluted if necessary with water, and make up to 65 grms. with water; (*b*) 30 grms. of zinc acetate in 3 grms. of the above acetic acid, and make up to 65 grms. with water. Mix, cool to 20° for 2 hours, and filter off any precipitate (due to sodium present as impurity in the reagents). When used as a reagent for the Drop Reaction, the proportions given on p. 131 should be taken.

Alkaloid Reagents.

Erdmann's Reagent.—Mix 6 drops of concentrated nitric acid with 100 c.c. of water, then take 25 drops of this solution and mix with 50 c.c. of concentrated sulphuric acid.

Froehde's Reagent.—Dissolve 0·1 grm. of ammonium molybdate in 10 c.c. of concentrated sulphuric acid.

Iodine in Potassium Iodide.—Dissolve 1 part iodine and 2 parts potassium iodide in 50 parts water.

Mandelin's Reagent.—Heat 0·5 grm. of vanadium chloride or oxide with 100 c.c. of concentrated sulphuric acid.

Potassium-Bismuth-Iodide (Dragendorff's Reagent †).—Dissolve 8 grms. bismuth nitrate in 20 c.c. nitric acid (1·18 sp. gr.), and dissolve 22·7 grms. potassium iodide in 40 c.c. water. Mix the bismuth solution with that of the potassium iodide with constant stirring. On standing and cooling, potassium nitrate crystallises out; pour off from the crystals, and make up to 100 c.c. with distilled water.

Potassium Mercury-Iodide (Mayer's Reagent).—13·6 parts mercuric chloride, and 50 parts potassium iodide dissolved in 940 parts of water.

Tannic Acid.—10 per cent. solution. This solution does not keep well, so should be made up in small quantities at a time.

Picric Acid.—Shake up crystallised picric acid with cold water till no more is dissolved, and filter from the undissolved portion

† This reagent is sometimes called "Thresh's Reagent".

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Where more than one reference is given, that in heavy type refers to the reactions of the substance or to the tables.